RATE DEPENDENCE AND SHORT-TERM CREEP BEHAVIOR OF PMR-15

NEAT RESIN AT 23 AND 288˚C

THESIS

Candice M. Westberry, 2nd Lt, USAF

AFIT/GAE/ENY/05-S07

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

RATE DEPENDENCE AND SHORT-TERM CREEP BEHAVIOR OF PMR-15

NEAT RESIN AT 23 AND 288˚C

THESIS

Presented to the Faculty

Department of Aeronautics and Astronautics

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

in Partial Fulfillment of the Requirements for the

Degree of Master of Science in Aeronautical Engineering

Candice M. Westberry, BS

2nd Lt, USAF

September 2005

RATE DEPENDENCE AND SHORT TERM CREEP BEHAVIOR OF PMR-15

NEAT RESIN AT 23 AND 288˚C

Candice M. Westberry, BS

2nd Lt, USAF

Approved:

_____   _____
Dr. Marina Ruggles-Wrenn (Chairman)   Date

_____   _____
Dr. Theodore Nicholas (Member)   Date

_____   _____
Dr. Anthony Palazotto (Member)   Date

Abstract

This research focuses on experimental investigation of rate-dependent behavior
and short-term creep of PMR-15 neat resin at 23 and 288ºC. Effect of loading rate on
monotonic stress-strain behavior was explored in monotonic tests at constant stress rates
of 0.75, 0.075, and 0.0075 MPa/s at 23 and 288ºC. In addition, effect of prior stress rate
on creep behavior was explored in creep tests preceded by uninterrupted loading to a
target stress. At each temperature three creep tests were conducted for a given stress
level, where loading rate was changed from test to test. Creep stress levels were 30 and
25 MPa at 23 and 288ºC, respectively. Also, the effect of stress and strain at the
beginning of the creep period was studied in stepwise creep tests, where specimens were
subjected to a constant stress rate loading with 1800 s creep periods at 5 MPa stress
intervals. Specimens were loaded to a maximum stress then unloaded to zero stress, with
creep periods during loading and unloading. Finally, the effect of loading rate was
studied in recovery tests where specimens were monotonically loaded to 30 MPa and
unloaded to zero MPa, then recovered for 12 hours.

Acknowledgements

I would like to thank the following people for their assistance during the course of my thesis: my faculty advisor, Dr. Marina Ruggles-Wrenn, for her guidance, support, and understanding throughout the course of this work, Dr. Greg Schoeppner (AFRL/MLBCM) and Dr. Richard Hall (AFRL/MLBCM) for their sponsorship of my thesis, Dr. Gyaneshwar Tandon (AFRL/MLBC) for providing the material panels, Barry Page for set-up and assistance with all test equipment, Jay Anderson for his technical support, Robert Jarusiewic for the timely machining of the specimens, and most importantly, my husband for being so supportive.

<div align="right">Candice M. Westberry</div>

Table of Contents

List of Figures

List of Tables

RATE DEPENDENCE AND SHORT TERM CREEP BEHAVIOR OF PMR-15 NEAT
RESIN AT 23 AND 288°C

I. Introduction

Polymer Material

Extensive research in polymer science has led to the development of high

performance plastics or engineering polymers. These polymers have properties that

approach those of metals, and can be used in traditional metal applications. They are of

great interest because of their high strength and low weight. Other characteristics include

corrosion and temperature resistance, as well as desirable electrical properties and design

flexibility.

These properties, especially the low weight, have made polymers particularly

attractive to the aerospace industry. High temperature polymer matrix composites

(HTPMCs) are strong candidates for applications such as aircraft engines, airframes,

missiles, rockets, and other weight sensitive systems. Decreasing the weight of a vehicle

can increase its range, payload, and/or performance. Therefore, a material that can lower

the weight of a vehicle becomes very important to US Air Force researchers.

High-temperature polymer matrix composites that are used in applications such as

turbine engines and high-speed aircraft skin are subject to extreme hygro-thermal

environments.   Failure of HTPMCs in these environments affects operational cost and

fleet readiness. These materials need to perform as reliably and predictably as their

metallic counterparts. Therefore, experimentally based and durability driven models are needed to predict how these materials will perform under realistic service conditions.

Experimental Investigation

Experimentation has long been used in all sciences and has led to significant advances in technology. The experimental data presents itself as a statement of fact. The phenomena actually happened and can be reproduced by repeating the experimental process. Experimentation is generally used to answer a question; what will happen if I do this? For example, in materials testing, an engineer wants to know how the material will react if a load is applied in a certain manner. Another question scientists ask is what do I have to do to get this end result? i.e. a cure for cancer. The experiment and the resulting data can be instrumental in answering these questions and/or leading the scientist in a direction that will. Sometimes the data leads the scientist to ask further questions. It is important that the experimental process and data be well documented so that the data can be reproduced and further steps can be taken toward the discovery of new scientific advances. The data from the experiments is carefully examined and used to propose various scientific theories. It is very important that there be a close correlation between theoretical and experimental data so that the theory can be used rather than experiments being done every time information is needed.

Types of Polymers

Polymerization reactions take place under extremely high pressure and with specific catalysts and/or initiators. There are two types of polymerization: addition and condensation. The former involves linking together thousands or hundreds of thousands of units called monomers without creating a by-product. Condensation polymerization is similar, but by-products are created in the process.

Based on melting behavior, polymers are also characterized as either thermoplastics or thermosets. Thermosets can be either liquid or solid at room temperature and can be solidified through heating or reacting with a specific compound. Upon heating, they do not melt. They burn or become charred. Thermoplastics tend to soften and become liquid with increased temperatures.

In addition, polymers can be characterized based on their molecular chains. Amorphous polymers have no order to their molecular chain make-up, while crystalline polymers do. Amorphous polymers, also referred to as glassy polymers, have a glass transition point, rather than a melting point that crystalline polymers have. Each of these types of polymers have their own advantages in physical properties and processing characteristics.

Some Examples of Phenomenologically Based Constitutive Models

Significant research in the study of polymer mechanical behavior has been accomplished in recent years. Some of these studies focused on rate sensitivity and creep behavior. Some explored relaxation, recovery, and history dependence as well.

Material is said to exhibit rate sensitivity when inelastic flow is fully established if an increase in loading rate results in an increase in stress level (or flow stress). Creep tests reveal deformation (strain) behavior under constant load conditions. Relaxation experiments elucidate stress response under constant displacement. Recovery refers to the ability of polymers to partially "recover" strain upon reaching zero load from any prior deformation. History dependence studies explore whether deformation behavior of the material depends on prior loading history. All of these experimental investigations serve to establish qualitative features of the deformation behavior of solid polymers. Krempl (1998) used these experimentally established properties of solid polymers to evaluate several "clock" models. The results showed that "clock" models generally based on linear viscoelasticity could not accurately represent the behavior of polymers. Specifically "clock" models cannot account for non-linear stress-strain behavior upon unloading, rate dependence, significant recovery at zero stress, and ability to accumulate creep strain well within the quasielastic region. A different model was needed to accurately represent these behavioral features found in polymers.

Further research compared the inelastic behavior of polymers to that of metals (Krempl and Khan, 2002). The study found that the two classes of materials were similar in that they both exhibit nonlinear creep including various creep regimes, and nonlinear rate sensitivity. Krempl and Khan (2002) and Colak (2005) also found that the nonlinear rate sensitivity, nonlinear unloading, creep, and recovery at zero stress could be accurately reproduced using a state variable model called viscoplasticity based on overstress (VBO).

It is instructive to revisit the basic constitutive models such as elasticity and viscoelasticity before introducing the VBO.

Linear elasticity postulates that the stress is linearly proportional to the strain. A linear elastic solid can be schematically represented by a spring element. The force applied to a spring is linearly proportional to its displacement. When the force on the spring is removed, the spring returns to its original state (zero displacement). This is also true for a linear elastic solid. When the stress on the material is returned to zero, the strain will return to zero as well.

Classic plasticity is the mathematical theory of time-independent irreversible deformation. Elastic-perfectly plastic solid exhibits linear elastic behavior before the threshold stress σ_s is reached. For stresses less than σ_s, deformation is fully reversible. Once the threshold stress is reached, stable permanent deformations develop.

In the case of linear elastic solid, reversibility of deformation is instantaneous. Once the load is removed, the deformation "disappears". Conversely, in the case of viscoelastic solid the recovery of deformation is "delayed" and is achieved only after some time. A simple analogical model of a linear viscoelastic solid consists of a linear spring element and a damper, connected in parallel (Kelvin-Voigt model). Alternatively, a three-element viscoelastic standard linear solid (SLS), where a spring element is connected in series to a Kelvin-Voigt model can also represent viscoelastic material behavior. A schematic of the standard linear solid is shown in Fig 1.
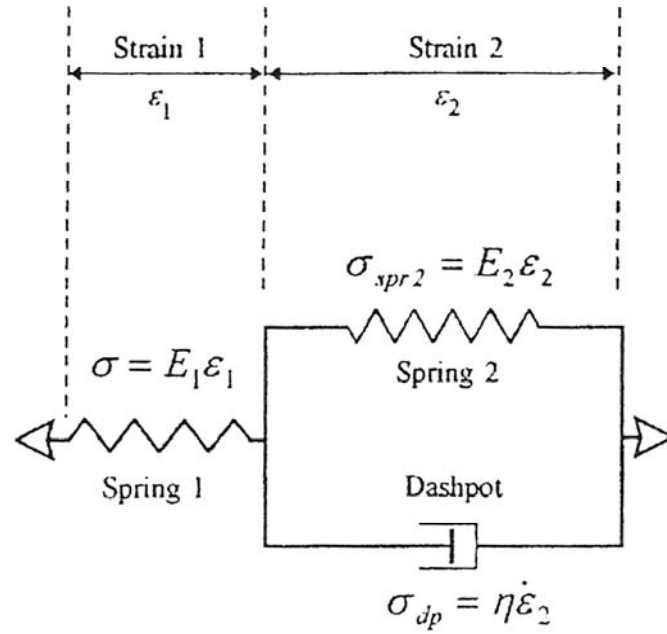
Figure 1. Schematic of the Standard Linear Solid (SLS) (Khan et al, 2002)

This model can reproduce strain rate sensitivity, creep, and relaxation behaviors on loading. However, it falls short at representing several behaviors that have been seen in polymers. The first is the hysteretic unloading behavior of polymers. This means that the loading and unloading curve creates a loop; in other words, the unloading curve does not follow the loading curve. This behavior upon unloading results in a loss of energy. The second is the change in sign of the stress rate during relaxation periods. The third is negative creep during unloading (the strain decreases during the creep period). The Viscoplasticity Based on Overstress (VBO) model was formulated based on the SLS. In the VBO, the Kelvin-Voigt element was modified as follows: (1) the spring was made non-linear and hysteretic, and (2) the viscous damper was made non-linear as well as dependent on the overstress (a modeling phenomena defined as the difference between

the stress and the equilibrium stress representative of the stress-strain behavior of the infinitesimally slow strain rate).

With this model, the elastic region is associated with a formulation of Hooke's law, and the inelastic behavior is associated with the increasing overstress. The overstress is the difference between the Cauchy stress (σ) and the equilibrium stress (g) (Figure 2). Polymers generally have a very small elastic region and large inelastic region. Krempl and Bordonaro (1992) found that VBO could accurately represent strain rate dependence, relaxation and creep response for Nylon 66. They also found that strain rate affected creep and recovery behavior.
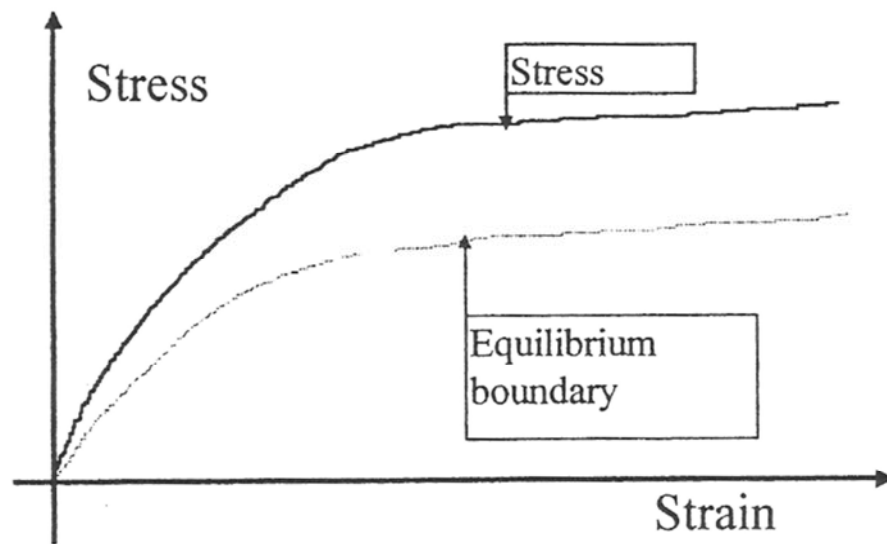
Figure 2. Schematic showing the stress-strain diagram and the equilibrium boundary, the stress that can be sustained at rest (Krempl et al,1998)

Khan (2002) studied the applicability of VBO to six different polymers: polycarbonate (PC), Nylon 66, high-density polyethylene (HDPE), polyethylene-terephthalate (PET), polyethersulfone (PES), and polyphenyl oxide (PPO). Three of these are amorphous polymers and the other three are crystalline polymers. He investigated rate sensitivity, creep behavior, relaxation behavior, and recovery behavior, all of which is commonly studied to relate polymers to VBO. He found that rate sensitivity was evident in all of the polymers tested and that it had an effect on relaxation and creep. He was able to successfully model creep, relaxation, and strain rate sensitivity of both HDPE and PPO.

These studies have been very significant to the understanding of the mechanical behavior of solid polymers. However, these studies were all performed at room temperature. Little research has been done on polymers at high temperature. Yet understanding mechanical behavior of polymers at high temperature is imperative if polymers are to be used in high temperature applications.

The Task at Hand

The PMR-15, of the Polymerization of Monomeric Reactant (PMR) family of polyamides, was developed in the 1970s at the NASA Lewis Research Center. It is one of the most widely used, high-temperature, thermo-setting polyamide resins used in aircraft engine components mainly because of its ease of processing, low cost, good stability, and performance temperatures up to 288ºC. PMR-15 is an amorpous polymer. This polymer is used as a matrix for composites.

The objective of this thesis is to investigate deformation behavior of PMR-15 at room temperature and 288ºC. Results provide a foundation for development of predictive models and methodologies. More specifically, results will determine whether a coupled damage/viscoelastic constitutive formulation can be used to model the material behavior or whether a thermodynamically-based viscoplasticity/damage constitutive framework must be employed. These results are critical to predicting and ensuring structural integrity of components made with PMR-15 based composites.

This study investigates (1) the influence of loading rate on stress-strain behavior, (2) the influence of prior stress rate on creep strain accumulated at a given stress during a given time period, and (3) the effect of prior loading history on creep strain and strain rate for a given time duration. These properties of deformation behavior are explored at 23 and 288˚C.

Mathematical modeling is not the primary focus of this thesis. Rather, this thesis will provide experimental basis for the mathematical modeling to follow in the future. The tests performed here are considered discriminating and were invented and/or employed when the viscoplasticity models for metals, VBO in particular, were under development. It is envisioned that similar modeling framework can be developed to represent behavior of PMR-15 polymers.

II. Experimental Arrangements

Material

The PMR-15 neat resin panels were provided by the Air Force Research Laboratory's Materials and Manufacturing Directorate. A high purity PMR-15 imidized foam, commercially available from Cytec Industries, Inc, was crushed into powder using a hydraulic press. Neat resin panels were made from the PMR-15 inidized powder. The panels were compression molded in the heat press. The curing cycle and post-cure cycle were similar to those described by McManus and Bowles (1998). Test specimens were cut from the polymer panels using a diamond saw.

Test Specimen

Test specimens with a reduced gage section (dogbone) geometry were used in this study. Specimen design and dimensions are shown in Fig. 3. Two groups of specimens of different gage section widths were machined according to the drawings in Fig 3. The width of the gage section was 12.7 mm for the fist group of specimens and 7.62 mm for the second group. Specimens from both groups produced consistent results. Neither specimen design exhibited bending due to extensometer pressure at elevated temperature. However, specimens with w = 12.7 mm. required higher loads to reach a given stress level than those with w = 7.62 mm. Such higher loads called for higher gripping pressure, which resulted in a large number of grip failures. Specimen design with w = 7.62 mm. is

recommended for subsequent studies. Note that in all tests to failure reported herein, the failure occurred within the gage section of the extensometer.
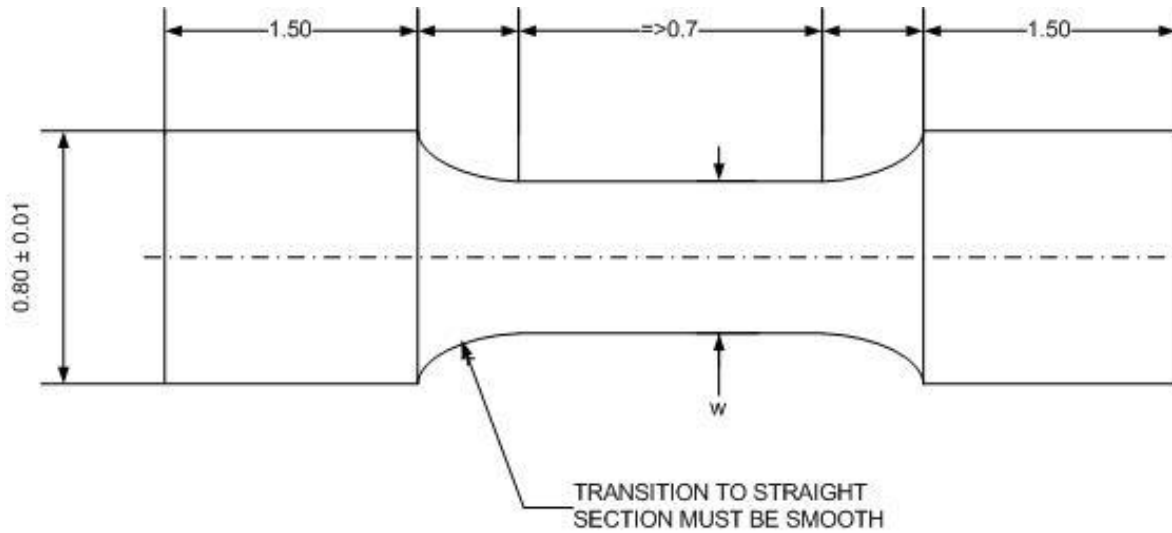
*Drawing not to scale

Figure 3. Test specimen. Dimensions are in inches

All test specimens used in this study were tabbed using a glass-fabric/epoxy material. Glass fabric/epoxy is a compliant material. This property reduces the stress concentration introduced by discontinuity at the tab end. Conversely, this material is also sufficiently tough to absorb the surface damage caused by the hydraulic wedge grips. The purpose of tabbing is twofold: (1) tabs transfer the load from the hydraulic wedge grips to the test specimen without causing stress concentrations due to uneven gripping surfaces, and (2) tabs protect the surface of the specimen from damage from the grips. Tabs were glued to the surface of the specimen using M-Bond 200 adhesive. Fig. 4 shows a side view of the specimen with the tabs on it. Two different thicknesses of tabs

were used. First, tabs with t = 0.94 mm, then tabs with t = 1.6 were used to accommodate for the high gripping pressure.
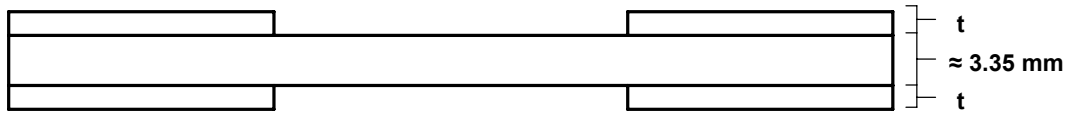
*Drawing not to scale

Figure 4. Side view of specimen with tabs

Test Equipment

A 5 kip (5000 lb) MTS (MTS Systems Corporation) axial servo hydraulic machine (configured horizontally) with MTS 647.02A-01 water-cooled hydraulic wedge grips were used in all tests. Two types of wedges were employed: (1) wedges with the contact surface coated with surf alloy and (2) wedges with a diamond patterned contact surface. Both types of wedges performed in a satisfactory manner. Low grip pressure of 1-1.5 MPa was used. Grip pressure was determined according to the procedure in the MTS grip manual. Standard MTS procedures and equipment were used to ensure and periodically verify grip alignment.
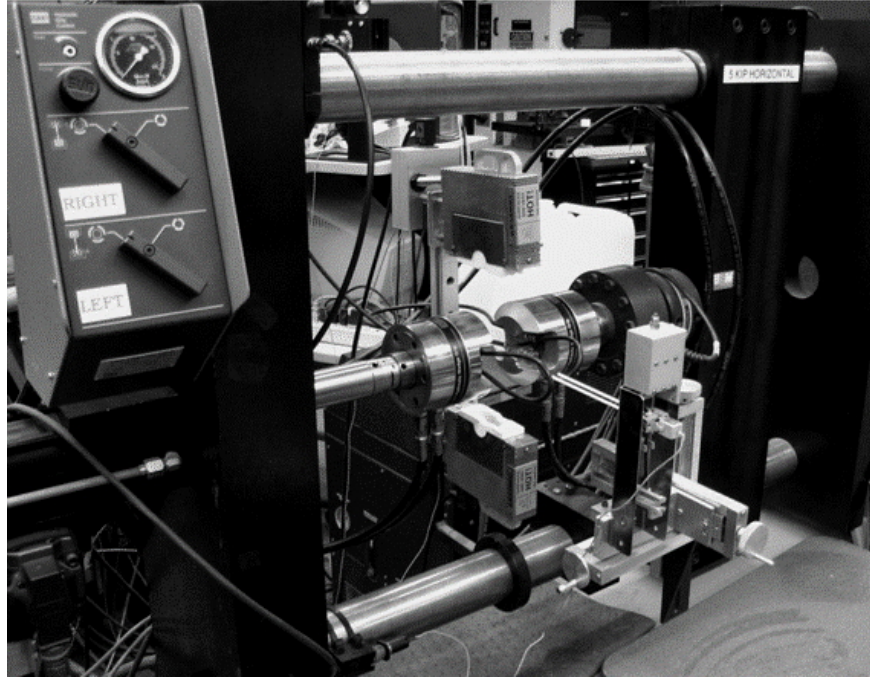
Figure 5: MTS Servo Hydraulic Machine

The MTS Test Star II controller was used for input signal generation and data acquisition. In room-temperature tests, strain measurement was accomplishment with an MTS extensometer, model 632.26B-30, with a gauge length of 7.62 mm. In elevated-temperature tests, an MTS high-temperature extensometer (model #632.53E-14, with a gauge length of 12.7 mm.) was employed.
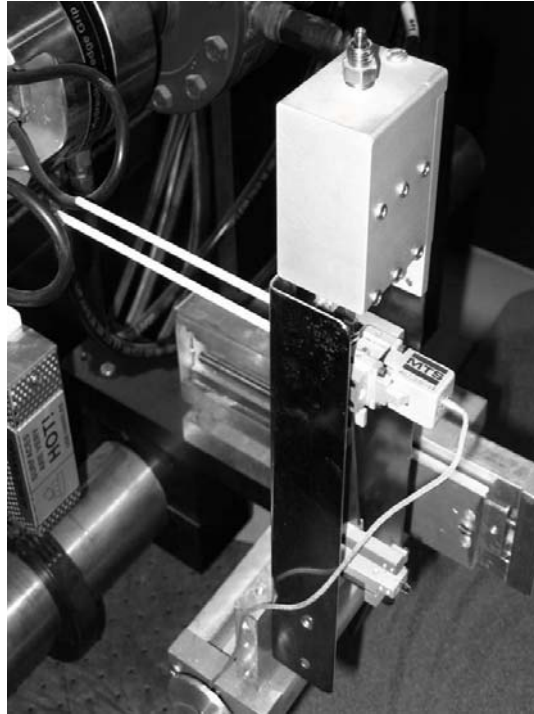
Figure 6. High temperature extensometer assembly

Testing at elevated temperatures was accomplished using an Amteco single-zone furnace, monitored with an S type thermocouple, and an MTS 409.83 Temperature Controller. Specimen temperature was monitored using two K-type thermocouples attached to the specimen with Kapton tape and a portable, two-channel temperature sensor (Omega Engineering, Inc. OMNI-CAL-8A-110). For the duration of the tests, the temperature remained within ±3˚C of the nominal temperature.

In elevated temperature tests, the furnace temperature was increased at the rate of 2˚C/min until the specimen temperature reached 288˚C. Specimen was then allowed to soak at temperature for 30 min. Once the specimen was thermally equilibrated, thermal strain was measured and the coefficient of thermal expansion determined. The strain was re-zeroed prior to the mechanical test.

Test Procedures

Monotonic Tensile Tests

The displacement-controlled tension tests were performed with a constant rate of 0.025 mm/sec. The stress-controlled tension tests were performed at constant rates of 0.75, 0.075, and 0.0075 MPa/s. In reality, the load was controlled. The conversion from load to stress rate was calculated by $\dot{P} = \dot{\sigma}A$ where $\dot{P}$ is the load rate, A is the specimen cross sectional area, and $\dot{\sigma}$ is the stress rate. All tests were performed in laboratory air.

Constant Stress Creep Tests

All creep tests were conducted in load (stress) control. A specimen was loaded to the desired creep stress level at a constant stress rate, then held at creep stress for the duration of 6 h. Constant stress rates of 0.75, 0.075, and 0.0075 MPa/s were employed for the loading portion of the test.

Stepwise Creep Tests

A stress-controlled stepwise creep test combines monotonic loading and unloading at a constant stress rate test with 1800 s creep periods. Figure 7 illustrates the idea behind this. Specimen is loaded to a certain maximums stress, then unloaded to zero stress. During loading and unloading, intermittent creep tests are introduced at 5 MPa stress intervals. Maximum stress was 35 MPA at 23°C and 30 MPa at 288°C. Monotonic loading and unloading rates of 0.75, 0.075, and 0.0075 MPa/s were used.

15
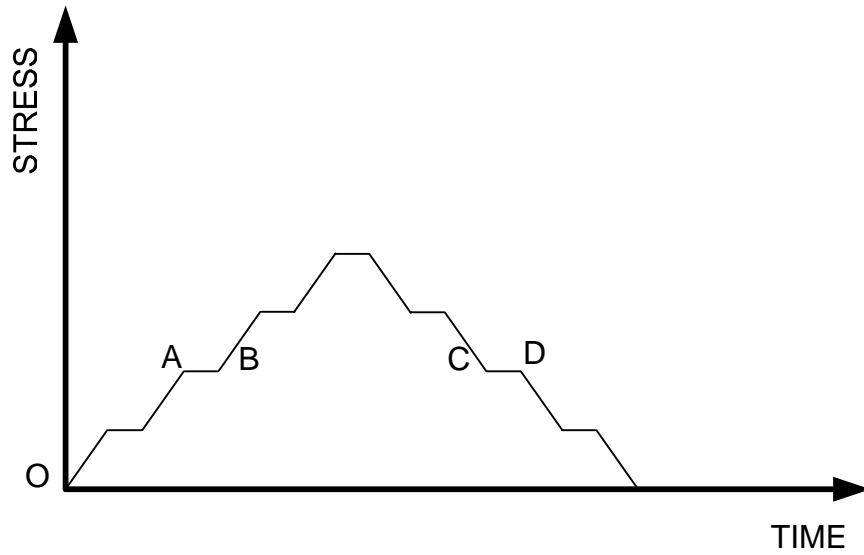
Figure 7. Schematic of stepwise creep test

Data Collection

In all tests, time, displacement, load, strain, and command signal were measured and recorded. All of these were measured by the equipment and automatically recorded into a file during the test. The engineering strain is a measure of the elongation divided by the original extensometer gage length, $\frac{\Delta L}{L}$ (measured by the extensometer). The load was used to find stress. Stress is simply the load divided by the original specimen cross sectional area $\frac{P}{A}$. The units of this figure are $\frac{N}{m^2}$ (Pa). In order to have stress in units of Megapascals (MPa), this number was divided by 1,000,000. Data acquisition intervals used in the monotonic tension tests were determined based on stress rate (see Table 1). In creep tests, data acquisition interval during loading (unloading) was determined as in

monotonic tests. During the actual creep periods, data was recorded every at an arbitrary

value of 3s which turned out to be sufficient enough to produce useful graphs.

Table 1. Time between data points based on stress rate

Stress Rate (MPa/s)	Time Between Data Points (s)
0.75	0.1
0.075	0.5
0.0075	3.0

III. Results and Discussion

Displacement-Controlled Experiments

Two monotonic tension tests to failure were conducted in displacement control with the constant rate of 0.025 mm/s. The objective was to determine stress and strain rates equivalent to a displacement rate used in typical tensile tests. Results are presented in Table 2, where ultimate tensile strength (UTS) (see Fig. 8), failure strain, and test duration, are given for each specimen together with equivalent stress and strain rates. The equivalent stress (strain) rates were calculated by dividing the UTS (failure strain) by test time. It is seen that the two specimens produced consistent results. An average of the two effective stress rates, namely 0.75 MPa/s, was used as a baseline loading rate in subsequent experiments.
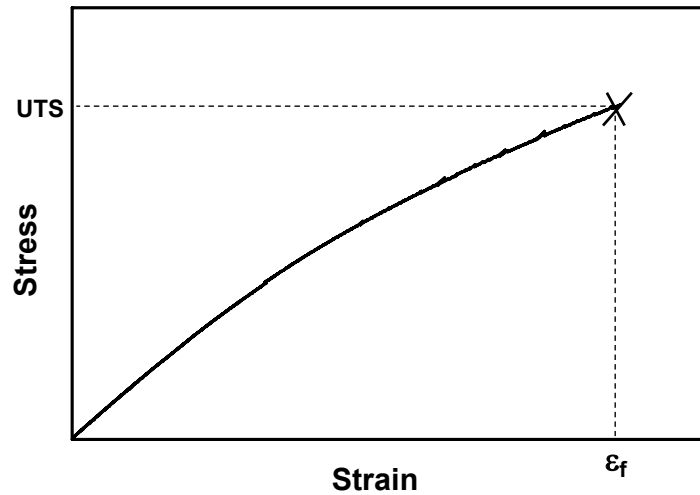
Figure 8. Schematic of UTS (stress at failure), and failure strain, ε_f, (strain at failure)

Table 2. Ultimate tensile strength, failure strain, test duration, equivalent stress and strain rates obtained in displacement controlled tensile tests

Specimen	UTS (MPa)	Failure Strain (%)	Test Duration (s)	Equivalent Stress Rate (MPa/s)	Equivalent Strain Rate (s⁻¹)
3	46.64	1.33	61	0.76	2.18×10^{-4}
4	52.1	1.78	71	0.73	2.51×10^{-4}

Two specimens were subjected to load (stress)-controlled monotonic tensile testing at the stress rate of 0.75 MPa/s. Results are presented in Fig. 9, where the tensile stress-strain curves produced in stress control are presented together with those obtained in displacement control. Results of these tests conducted in different control modes but with the same equivalent loading rate reveal that control mode has no effect on qualitative and insignificant effect on quantitative stress-strain behavior.
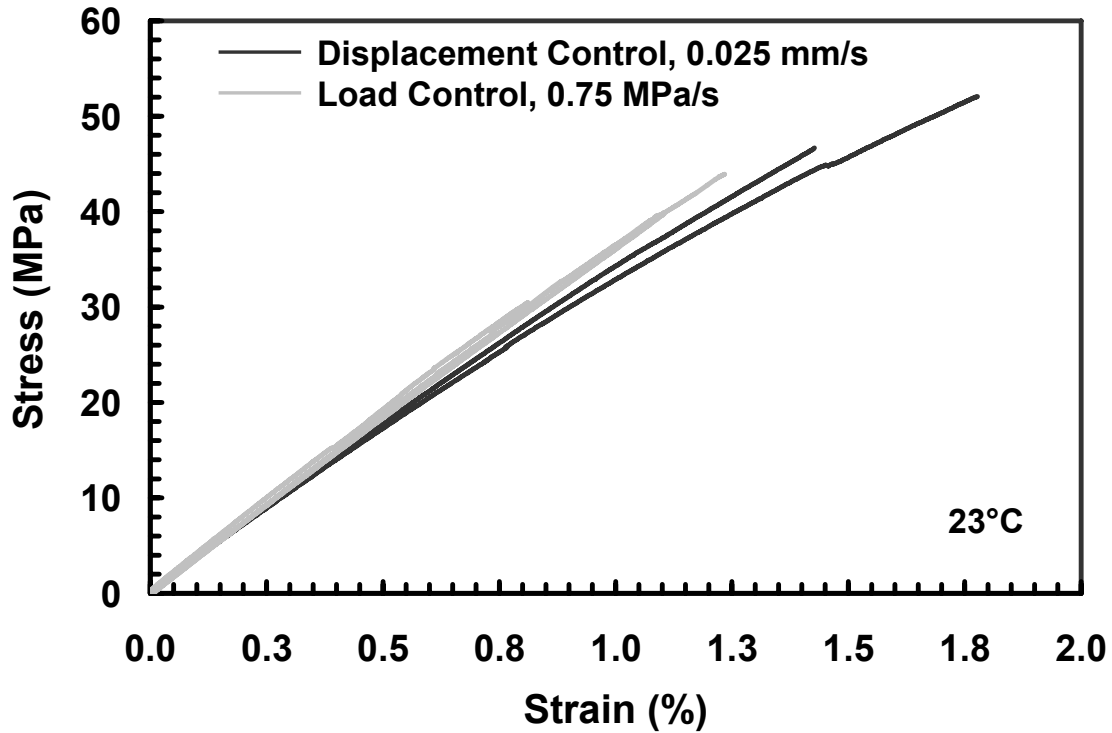
Figure 9. Tensile stress-strain curves produced in stress- and displacement-controlled tests with the loading rates of 0.75 MPa/s and 0.025 mm/s, respectively

Effect of Loading Rate on Monotonic Stress-Strain Behavior at 23 and 288°C

Effects of loading rate were investigated in experiments where the loading rate was changed by an order of magnitude from test to test. Tests were conducted in stress control and stress rates of 0.75, 0.075, and 0.0075 MPa/s were employed. The experiments were performed both at 23 and 288°C. Typical stress-strain curves obtained at 23°C are presented in Fig. 10.

Figure 10. Stress-strain curves for PMR-15 neat resin at three different stress rates at 23°C. Nonlinear rate sensitivity is apparent

It is seen that the stress-strain curves obtained under various constant stress rates show very little if any dependence on rate leaving the origin. However, after transition to the inelastic range where the slope becomes less than the elastic slope, the stress-strain curves obtained at different loading rates become distinctly different. In order to assess rate dependence, the stress (strain) levels at the same strain (stress) obtained with different loading rates must be compared. Results in Fig. 10 reveal that in tests conducted with the loading rates of 0.75, 0.075, and 0.0075 MPa/s, the flow stresses corresponding to a strain of 1.0% were 36.2, 33.0, and 30.5 MPa, respectively. A tenfold increase in the loading rate causes much less than a tenfold increase in the flow stress. Conversely, the strain levels obtained at a given stress of 40 MPa at 0.75, 0.075, and

0.0075 MPa/s are 1.11 %, 1.24 %, and 1.33 %, respectively. Once again, a nonlinear effect of the loading rate is apparent.

The stress-strain curves obtained at 288°C are presented in Fig. 11. The effects of temperature on tensile behavior and properties are evident. Elastic modulus and UTS decrease dramatically with increasing temperature. However, the stress-strain behavior exhibits no influence of loading rate at 288°C. Stress-strain curves obtained at different constant stress rates are virtually indistinguishable. One test at 0.075 MPa/s accumulated much more strain than the others.
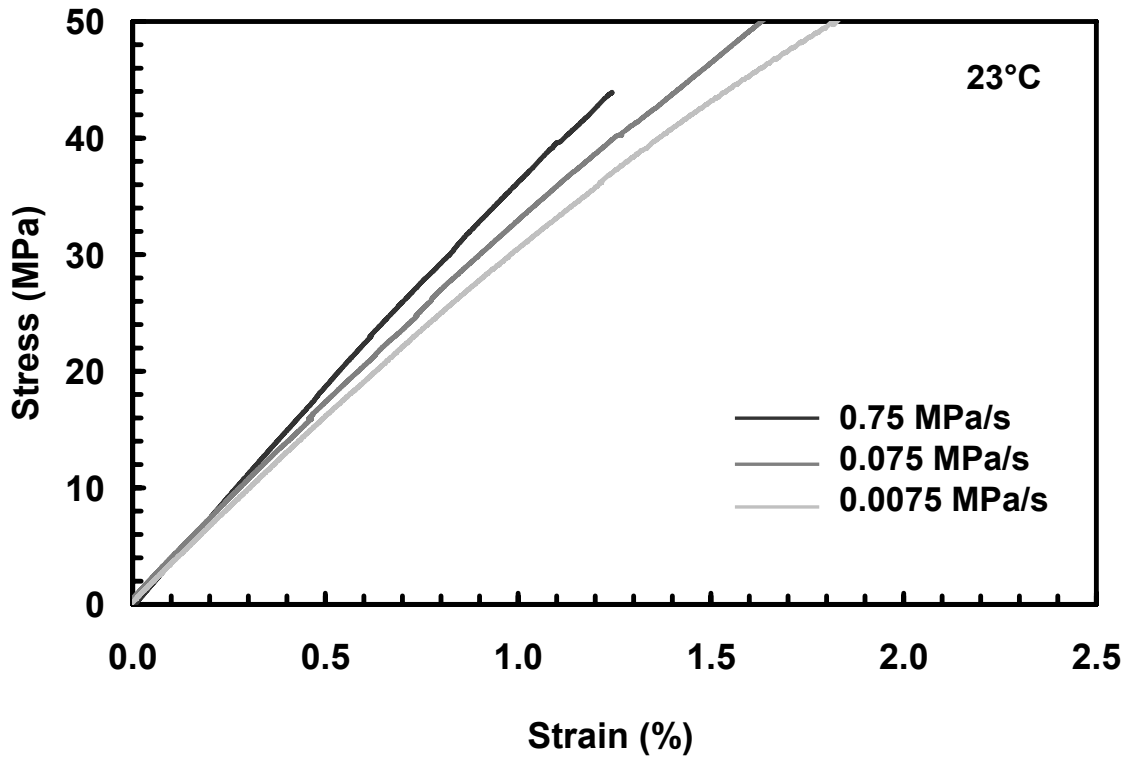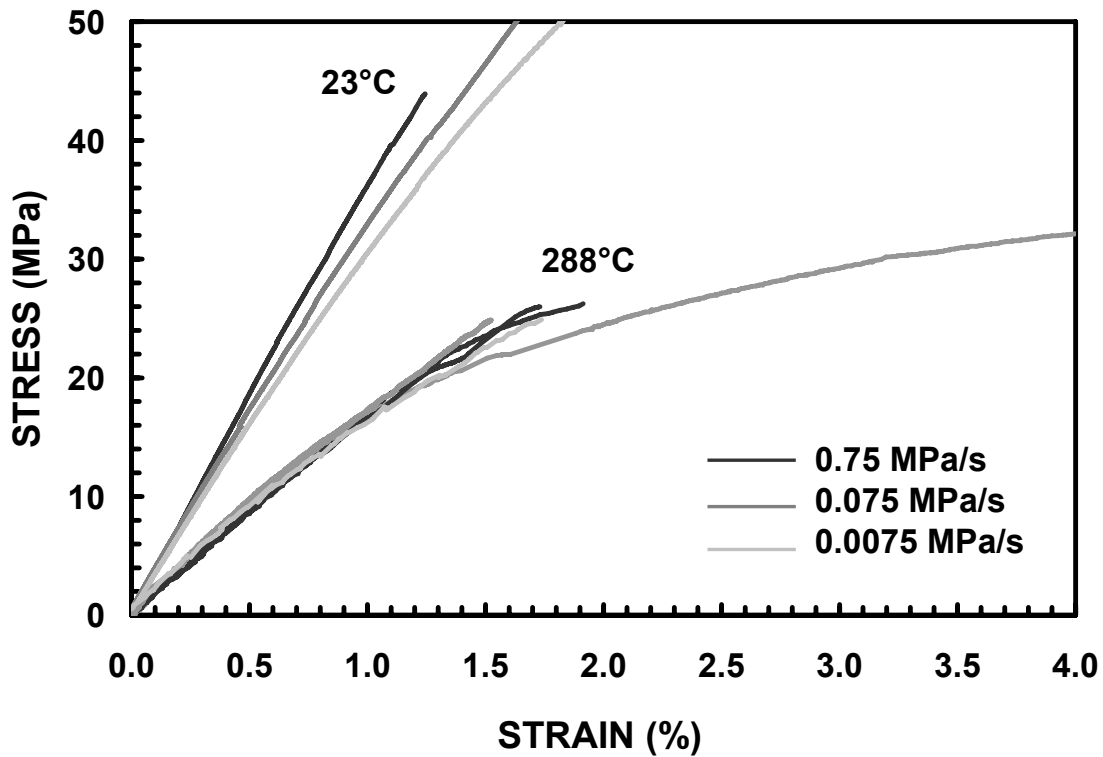

Figure. 11. Stress-strain curves for PMR-15 neat resin at three different stress rates at 23 and 288°C. The rate sensitivity, apparent at 23°C, is negligible at 288°C. Effect of temperature on tensile strength and stiffness is evident.

Monotonic Loading and Unloading Behavior

All rates were considered for monotonic (continuous) loading and unloading, but the curves for all rates exhibited similar features for each temperature, so only one test for each temperature will serve as the representative curve. Fig. 12 shows the representative stress-strain curve of monotonic loading and unloading for room temperature. The unloading curve is linear and follows almost the same path as the loading curve. This means that this material is still within the quasi-elastic region at 30 MPa at 23°. This was also true for both of the slower rates.
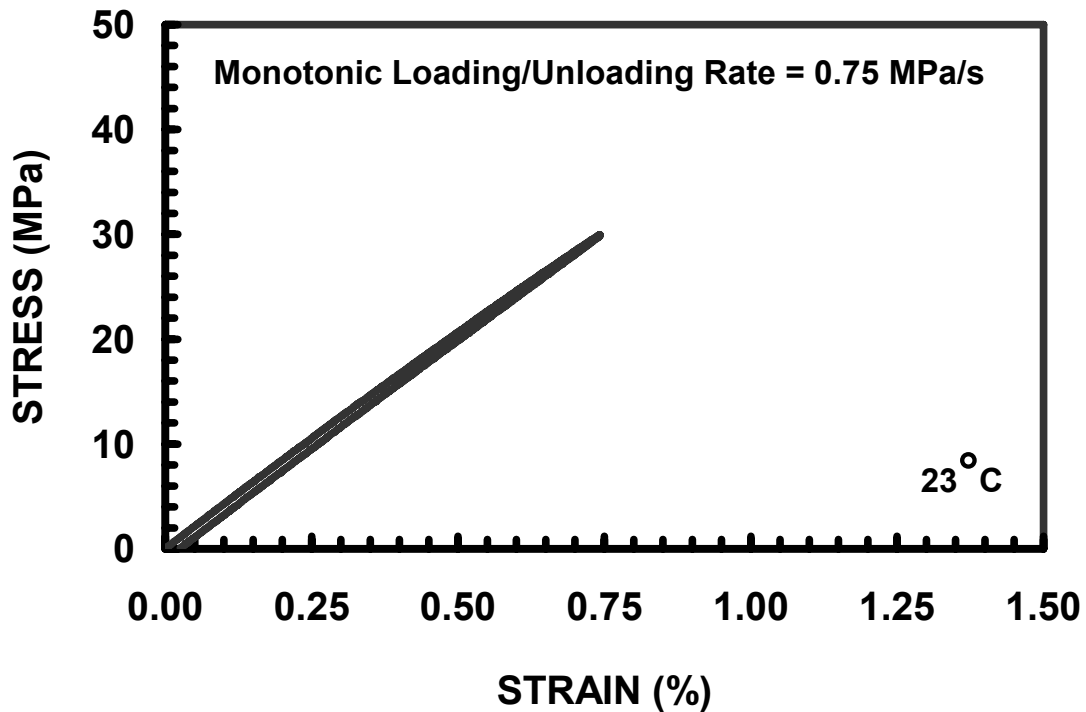
Figure 12. Representative monotonic loading and unloading stress-strain curve at 23ºC

Unloading for 288ºC was much different than at 23ºC (Fig. 13). The unloading

curve was initially non-linear meaning, as the stress decreased, the strain was still

increasing. Notice that the representative curve here is from the test conducted at 0.075

MPa/s. The tests conducted at 0.75 and 0.0075 MPa/s also had curved unloading. The

curved unloading, however, was less pronounced with the test conducted at 0.75 MPa/s

and more pronounced with the test conducted at 0.0075 MPa/s. The energy in the system

is defined as the area under the stress strain curve. This means that there is less energy in

the system upon unloading. Therefore, the area between the loading curve and the

unloading curve represents the energy lost (or rather transferred to some other form).
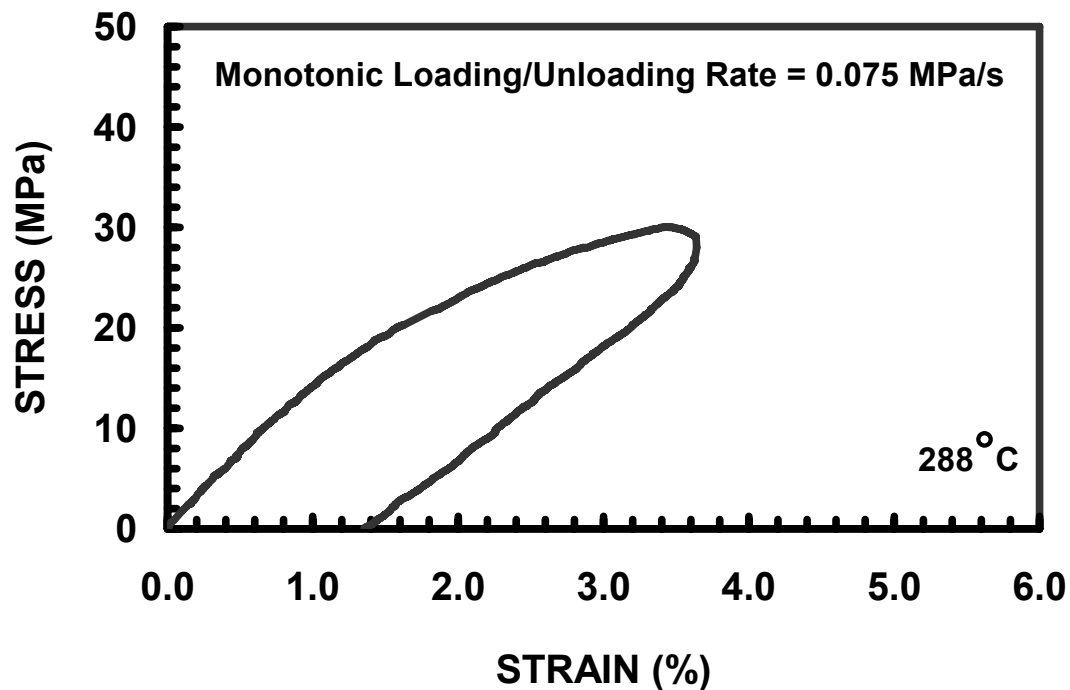

Figure 13. Representative monotonic loading and unloading stress-strain curve at 288ºC

Effect of Loading Rate on Creep Behavior at 23 and 288ºC

Effect of prior stress rate on creep behavior was explored in creep tests preceded by uninterrupted loading to a target creep stress. At each temperature three creep tests were conducted for a given stress level, where loading rate was changed from test to test. Creep stress levels were 30 and 25 MPa at 23 and 288°C, respectively.

In tests performed at 23°C (288°C), the stress was first increased monotonically to 30 MPa (25 MPa), and then held constant for a period of 6 hours (21,600 s). Three tests, where monotonic loading rate varied from test to test, were conducted at each temperature. Monotonic loading rates were 0.75, 0.075, and 0.0075 MPa/s. Results are presented in Figs. 14 and 15 for 23 and 288°C, respectively.

As seen in Fig. 14, the material exhibits both primary (creep strain rate is decreasing) and secondary creep (creep strain rate is constant) in all tests conducted at 23°C.   However, creep behavior shows little if any effect of prior stress rate, similar creep strains were measured in all tests. Creep strains accumulated in tests with prior stress rates of 0.75, 0.075, and 0.0075 MPa/s are 0.1, 0.1 and 0.085%, respectively. The creep strain is defined as the strain accumulated in the creep period only (measured strain minus the strain at the beginning of the creep period).
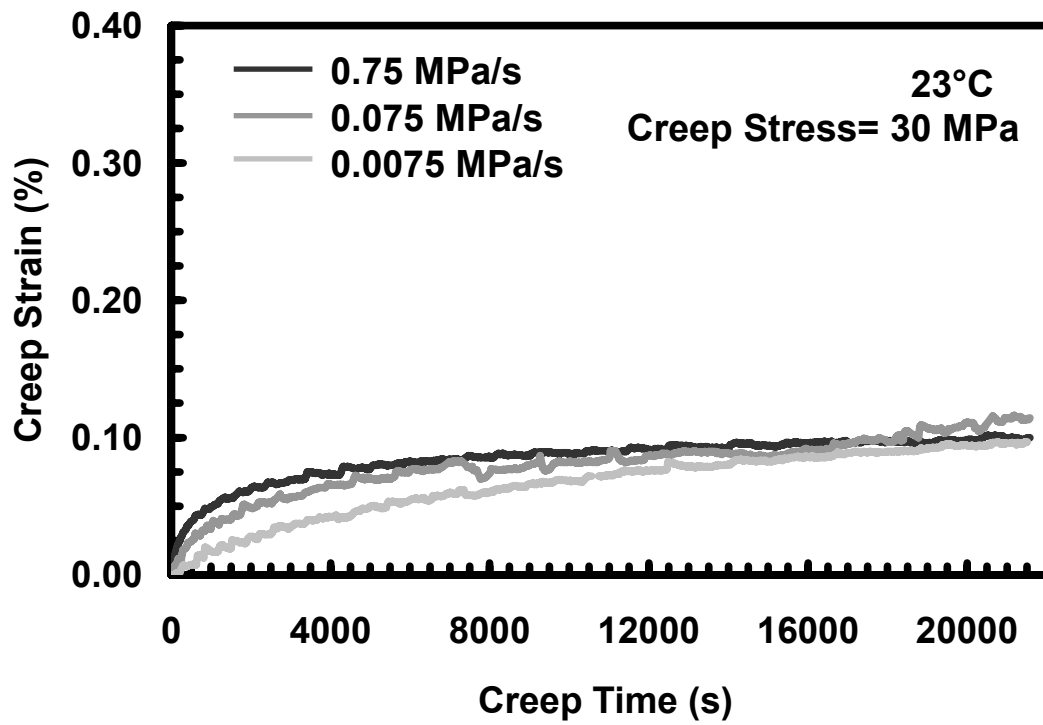
Figure 14: Creep strain vs. time at 30 MPa and 23°C. Prior stress rate has no significant effect on creep strain accumulation
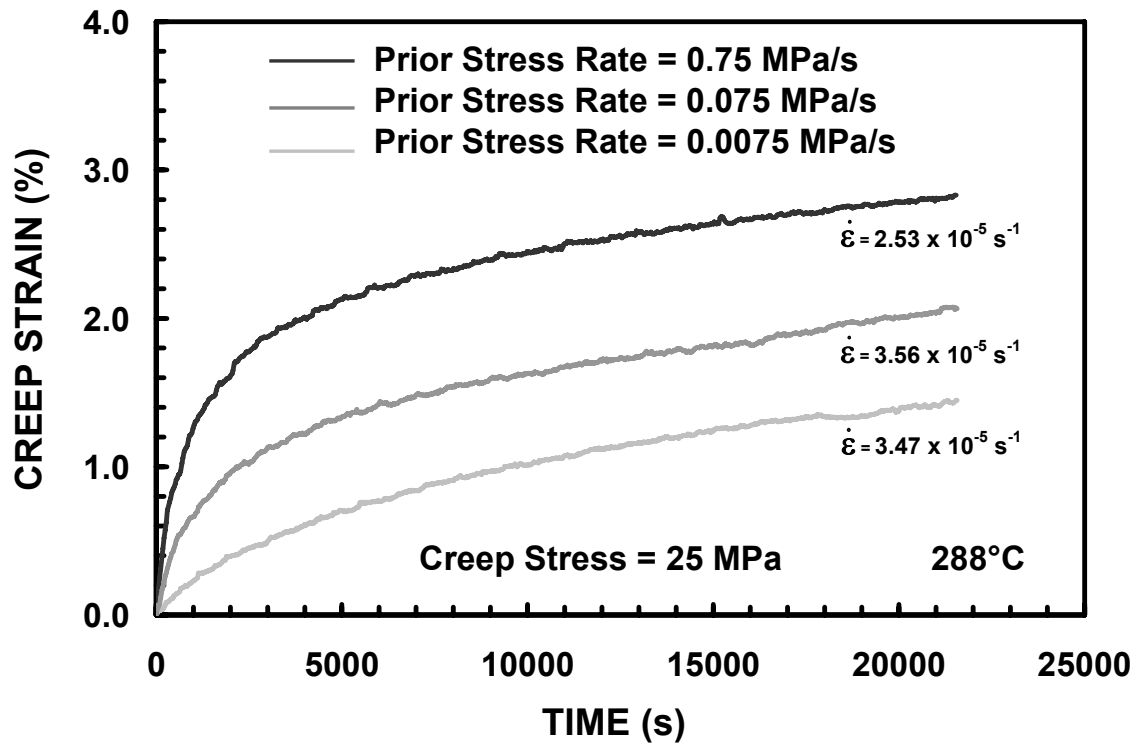
Fig. 15. Creep strain vs. time at 25 MPa and 288°C. Effect of prior stress rate on creep strain is apparent

Results in Fig. 15 show a noticeable effect of temperature on creep response. As expected, considerably larger creep strains were accumulated at 288 than at 23°C. Furthermore results in Fig. 15 demonstrate that at 288°C creep behavior is profoundly influenced by the prior stress rate. Despite the negligible rate dependence at 288°C observed in Fig. 11, the effect of prior stress rate on the creep strain is significant. Creep strain accumulations of 2.83, 2.06, and 1.45% were obtained in tests conducted with prior stress rates of 0.75, 0.075, and 0075 MPa/s, respectively. For a given stress level, creep strain accumulation increases nonlinearly with increasing prior stress rate. An increase of two orders of magnitude in prior stress rate results in an early twofold increase in creep strain. Primary and secondary creep regimes are apparent in all tests.

For each test, the minimum creep strain rate was calculated by examining the creep strain vs. time diagrams obtained in secondary (constant strain rate) creep regime, and determining the slope of these graphs. Portions of the creep diagrams used to determine secondary creep rate are shown in Fig. 16. During secondary creep, the relationship between creep strain and time is linear. The creep rate corresponds to the slope of the linear fit. Note that all tests shown in Fig. 15 achieved similar secondary creep rate. Conversely, the primary creep rate is significantly affected by the prior stress rate. Consequently, creep strains accumulated during primary creep are vastly different for different preceding stress rates.
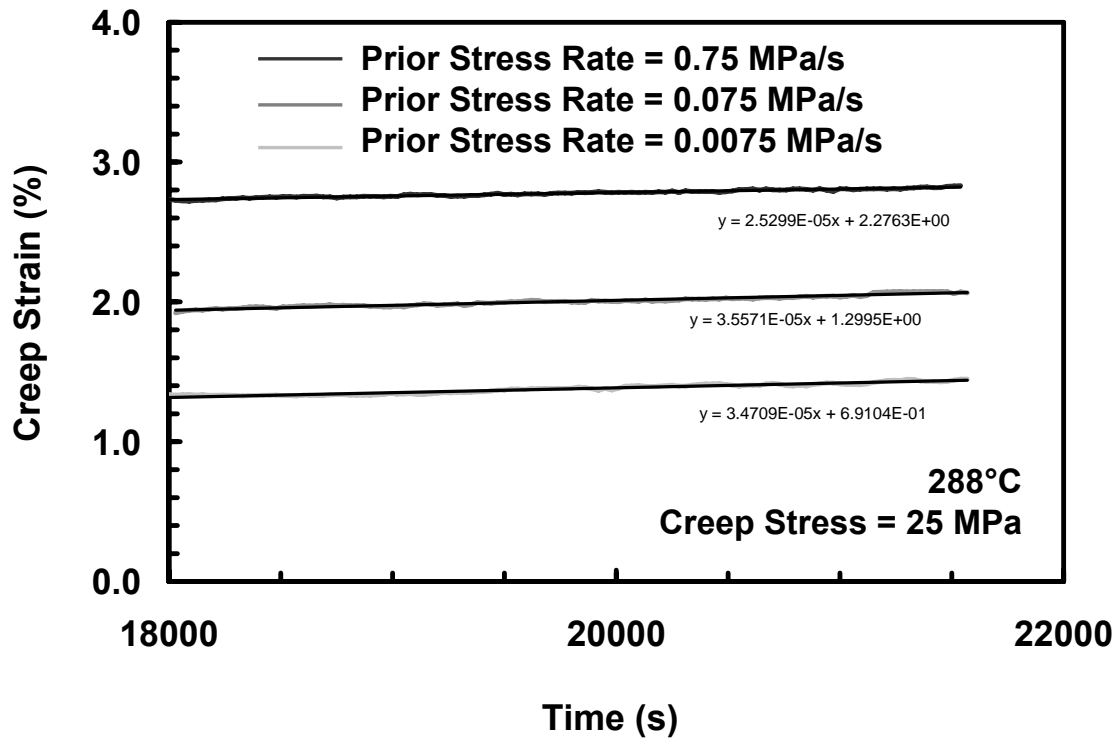

Figure 16. Portions of the creep strain vs. time graphs used to determine the minimum creep rates

The observations presented above lead to an important conclusion. The amount of creep strain for a given hold time does not depend on the stress alone. Therefore it is not sufficient to merely state a stress level when presenting creep results, prior stress rate must be accounted for as well.

Creep Behavior during Loading and Unloading at 23 and 288ºC

It is recognized that creep behavior may be influenced not only by the stress level but also by the strain at the beginning of the creep test. Furthermore, creep behavior during unloading may be significantly different from that during loading. In order to investigate these phenomena, a stepwise creep test was performed, where a specimen was subjected to a constant stress rate test with 1800 s creep periods at 5 MPa stress intervals. In this test, a specimen is loaded to a certain maximum stress, then unloaded to zero stress, with creep periods introduced both during loading and unloading. Maximum stress was 35 MPa at 23°C and 30 MPa at 288°C. Three stepwise creep tests with monotonic loading rates varying from tests to test were performed at each temperature of interest. The stress rates of 0.75, 0.075, and 0.0075 MPa/s were employed.

The stress-strain curve obtained in a stepwise creep test performed at 23°C with the monotonic loading rate of 0.75 MPa/s is shown in Fig. 17 together with the stress-strain curve obtained in an uninterrupted tensile test conducted at the same stress rate. In addition, creep strain vs. time curves are presented in Fig. 18.
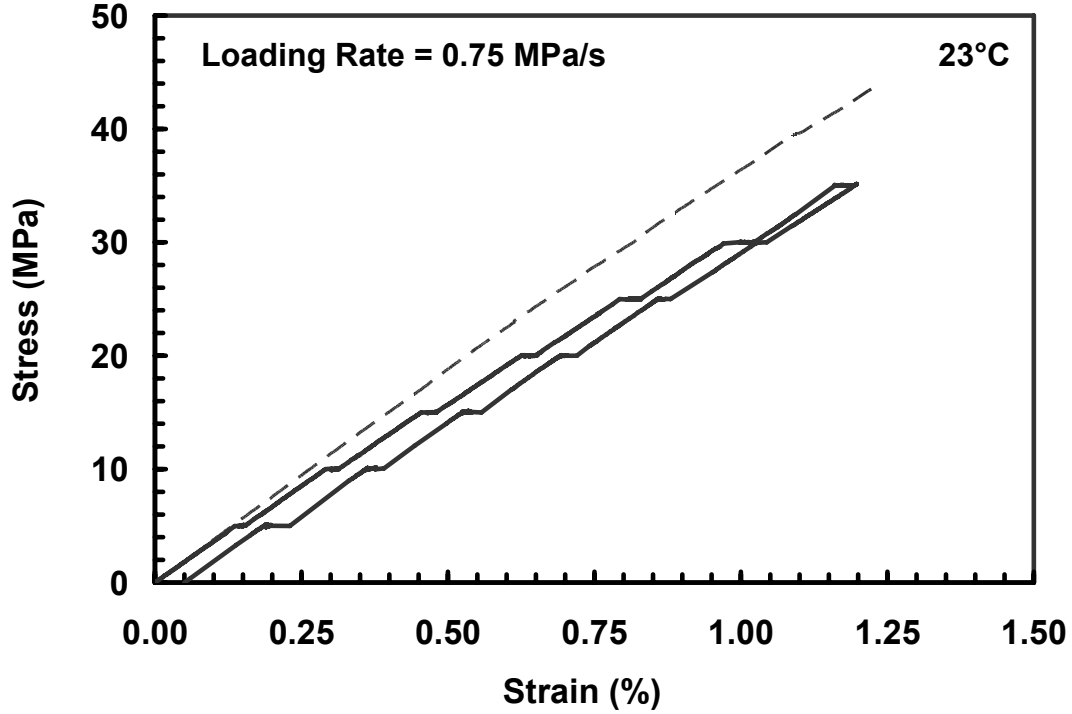
Figure 17: Stress controlled test conducted at the rate of 0.75 MPa/s with intermittent creep periods of 1800 s duration at 23°C. At the same stress level the creep rate is different during loading and unloading. Negative strain rates are observed in creep tests during unloading. Dashed line is an uninterrupted stress-strain curve

Results in Figs. 17 and 18 reveal that creep is observed at stress levels that are well within quasi-elastic region of the stress-strain diagram. Creep regime is primary. All creep strains are small (the largest creep strain is ≈ 0.05%). Upon loading, creep develops gradually as the stress level of the creep test increases to 30 MPa. Creep strain increases with increasing creep stress. It is noteworthy that more creep strain is accumulated at 30 MPa that at the higher stress of 35 MPa. Such unusual response can be readily explained within the framework of the Viscoplasticity Based on Overstress (VBO). At the conclusion of the 20 MPa creep test, stress rate controlled loading resumes, but does not continue long enough to allow the stress-strain curve to reach the dashed line. The stress-

strain curve is now considerably to the right of the dashed line. In the light of the VBO, this indicates that at the stress level of 30 MPa the overstress (which is responsible for creep deformation) would be higher in the uninterrupted test than in a stepwise creep test. After the 30 MPa creep period is completed, the stress-strain curve falls even further to the right of the monotonic curve (the dashed line). According to the VBO, the overstress would be higher at the start of the 30 MPa creep test than at the start of the 35 MPa creep period. Higher overstress results in higher creep strain rates and creep strain accumulations.

Results obtained during the 30 MPa creep period of the stepwise creep test were compared to those of the creep test preceded by uninterrupted loading (at the same stress rate) to 30 MPa. Comparison is presented in Fig. 19. Strain accumulated in a creep test preceded by uninterrupted loading is 12% higher than that accumulated in a creep period of a stepwise creep test. Because creep strains accumulated in both tests are small, this difference in creep strains is somewhat obscured in Fig. 19. The overstress at the 30 MPa point in the uninterrupted stress-strain curve would be higher than that at the start of the 30 MPa creep period. Therefore more creep strain would be accumulated in a test preceded by uninterrupted loading.

It is seen in Figs. 17 and 18 that creep upon unloading is significantly different from creep during loading. Upon unloading, the first creep period shows negative creep (decrease in strain during the creep period). This phenomena, although seemingly unusual, has been observed in other polymers and also in metals (Krempl and Bordonaro, 1995; Khan and Krempl, 2004; Ruggles, 1994). The subsequent creep periods show a decrease in the strain that becomes larger as the creep stress level decreases to zero stress.

The creep curves in Fig. 18 reveal that all creep is primary. It is also seen that at the same creep stress level, the creep rate is different on loading and unloading. Furthermore, at the lower stress levels, the reverse creep at a given stress is more pronounced than creep during loading.
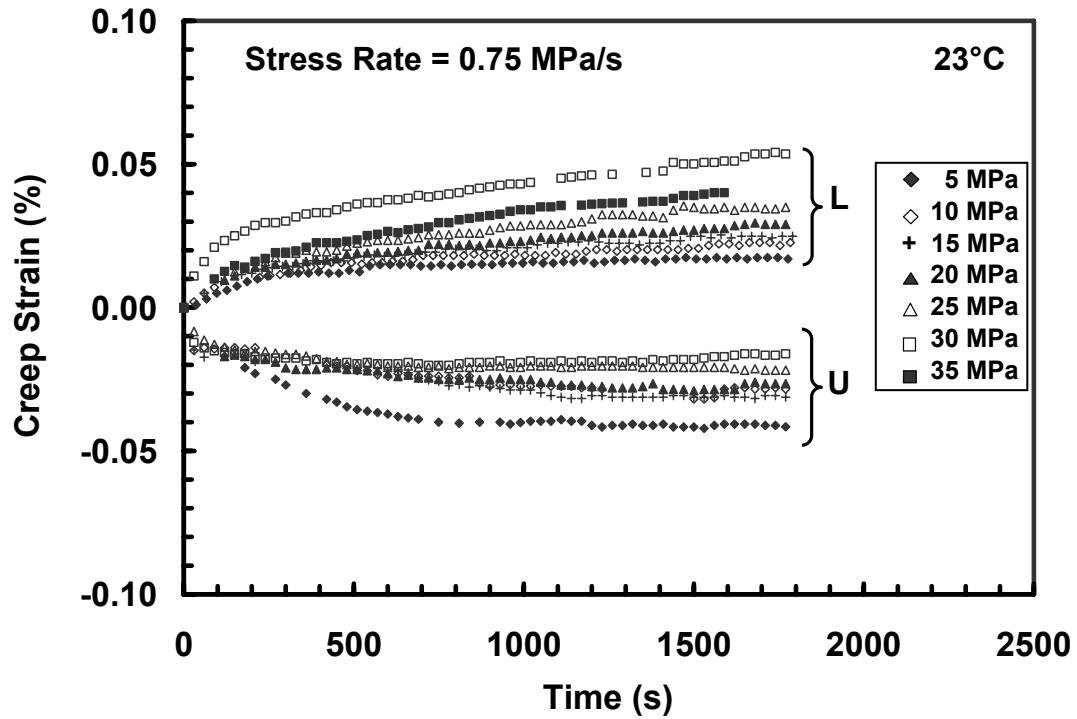

Figure 18. Creep curves pertaining to the test shown in Fig. 17. All creep is primary, except at 30 MPa, where both primary and secondary creep regimes are present. L = loading; U = unloading
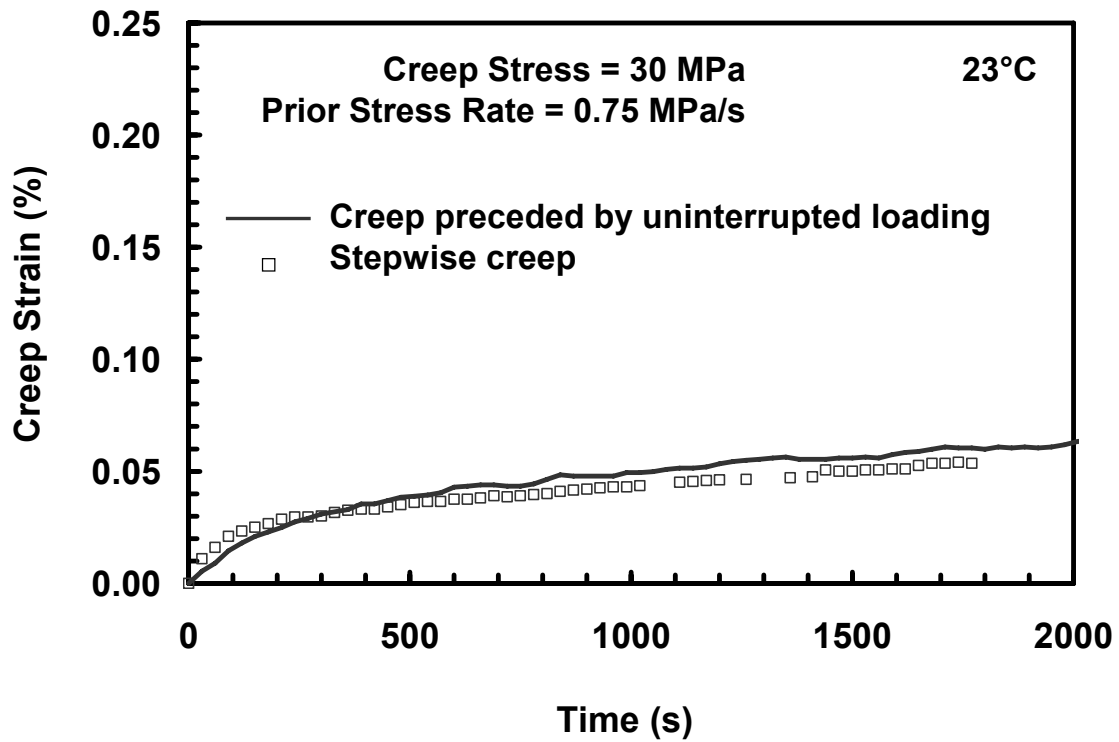
Figure 19. Creep curves obtained at 30 MPa in stepwise creep test and in creep test preceded by uninterrupted loading for stress rate of 0.75 MPa/s at 23ºC. Strains at the beginning of creep tests are 0.80 (creep preceded by uninterrupted loading) and 0.97% (stepwise creep)

Figures 20 and 21 show the results of the stepwise creep tests conducted with the stress rate of 0.075 MPa/s. Note that due to lower monotonic stress rate, creep strains are lower than those obtained in a stepwise creep test with the monotonic loading rate of 0.75 MPa/s. However, stress-strain as well as creep behaviors are qualitatively unchanged.

Figure 20. Stress controlled test conducted at the rate of 0.075 MPa/s with intermittent creep periods of 1800 s duration at 23°C.

Figure 21. Creep curves pertaining to the test shown in Fig. 20

When comparing results of the creep tests at 30 MPa for both stepwise and uninterrupted loading histories, it is seen that there is virtually no difference. This is not unexpected, since at 30 MPa the stress-strain curve of the stepwise test is very close to that of the uninterrupted test, indicating that the overstress for both tests is not significantly different.

Figure 22. Creep curves obtained at 30 MPa in stepwise creep test and creep test preceded by uninterrupted loading for stress rate of 0.075 MPa/s at 23ºC

The stress strain curve obtained in the stepwise creep test conducted with the monotonic stress rate of 0.0075 MPa/s is shown in Figure 23. In this case, as expected, lower stress rate resulted in lower creep strain accumulation. For example, at 30 MPa, the stepwise tests conducted with stress rates of 0.75 and 0.075 MPa/s accumulated 0.053 and 0.041% strain, respectively. Only 0.027 % strain was accumulated during the 30 MPa creep period in a stepwise test with the loading rate of 0.0075 MPa/s.
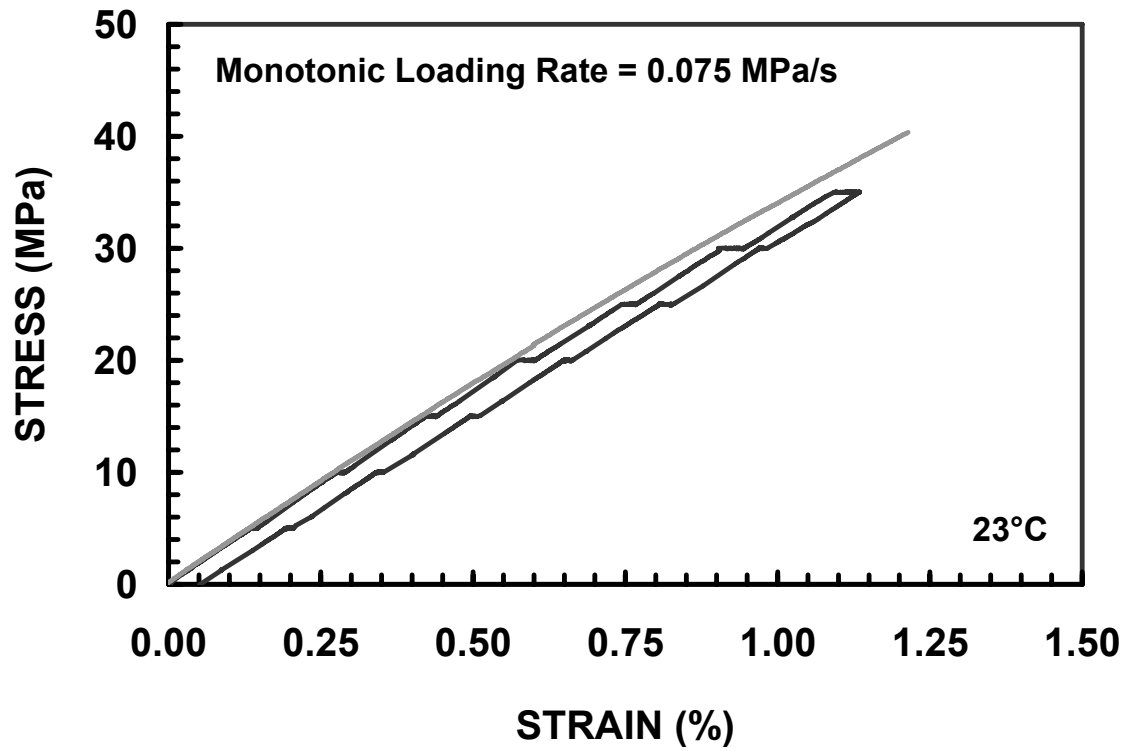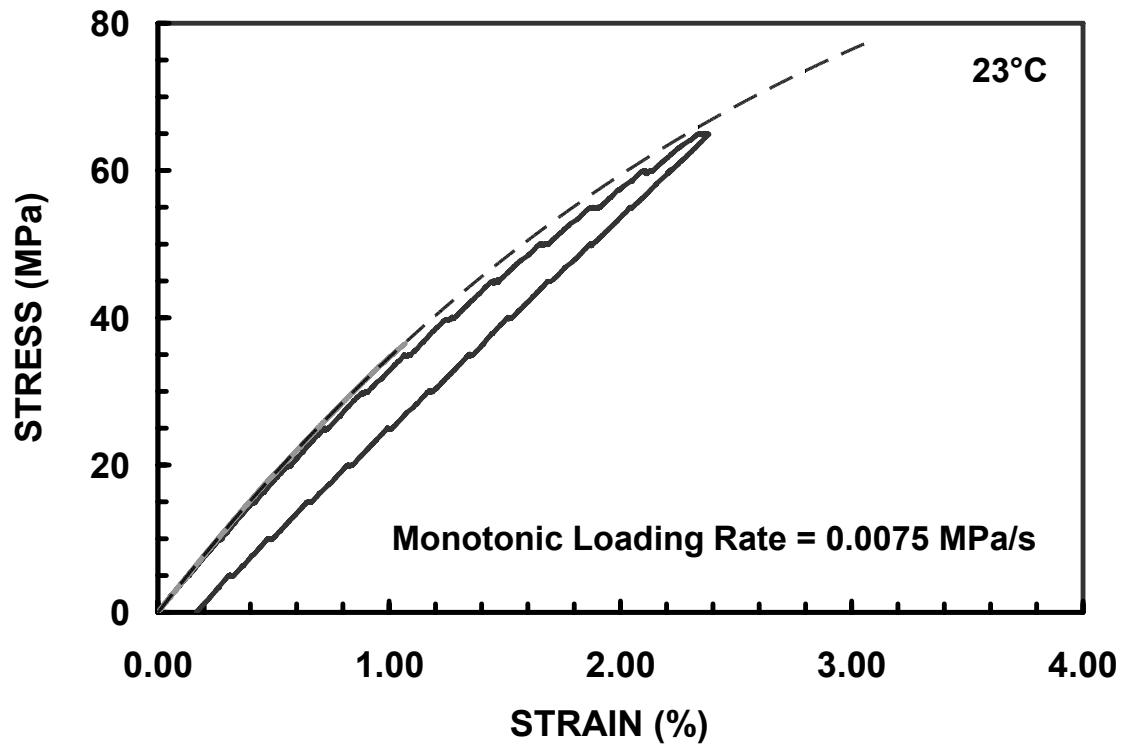
Figure 23. Stress controlled test at the rate of 0.0075 MPa/s with intermittent creep periods of 1800 s duration at 23°C
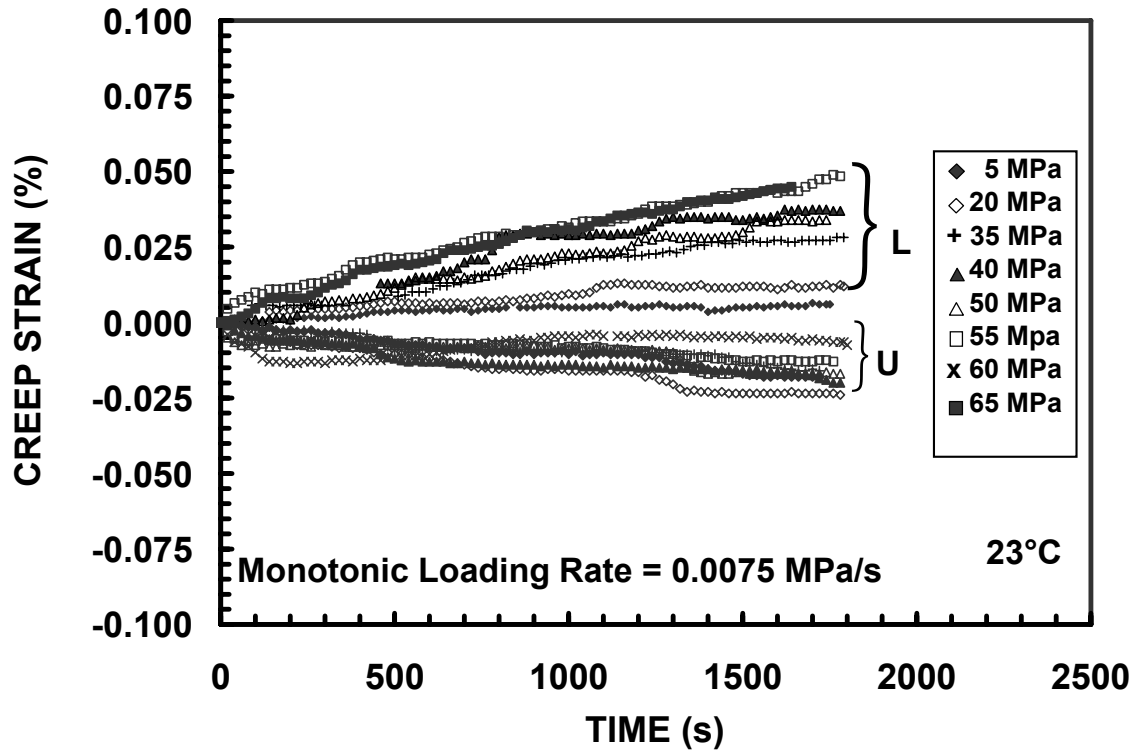
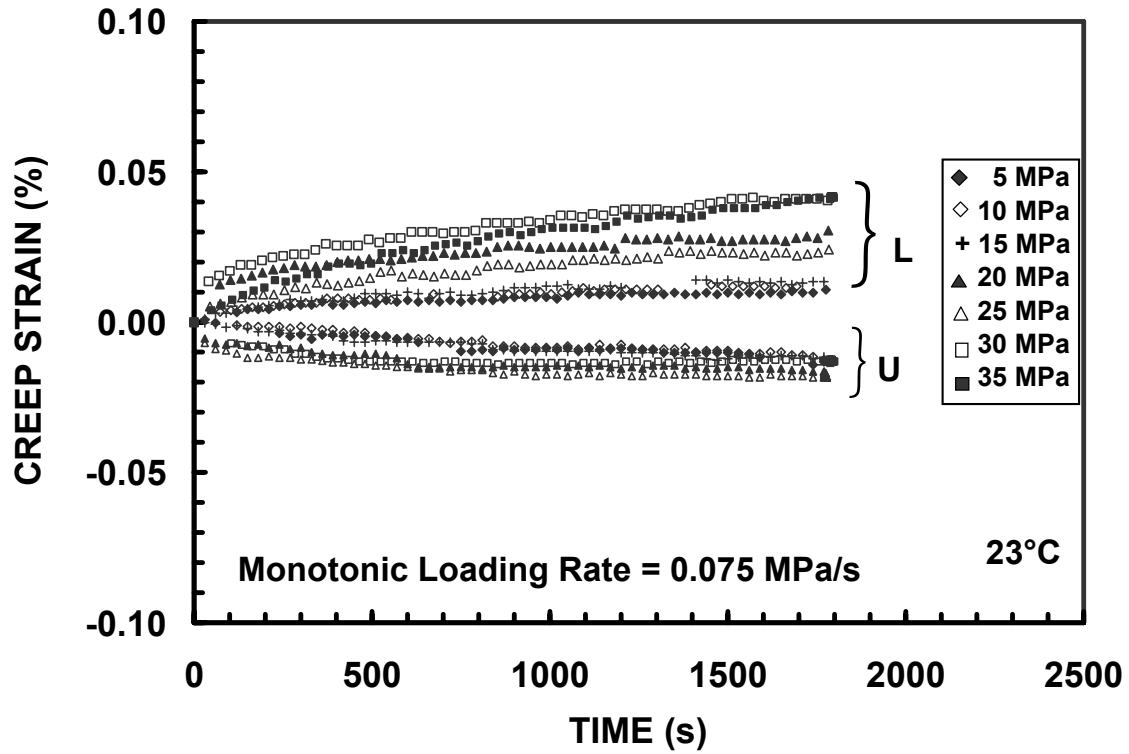Figure 24. Creep curves pertaining to the test shown in Fig. 23

Both the stepwise creep test and the uninterrupted loading creep test conducted with the stress rate of 0.0075 MPa/s accumulated very low creep strains. Note that the stress-strain curves of the stepwise creep test and uninterrupted tests (see Fig. 23) are very close, indicating similar evolution of the overstress in the two tests. This suggests that the strain accumulation should be equal. Figure 25 confirms that it indeed is.
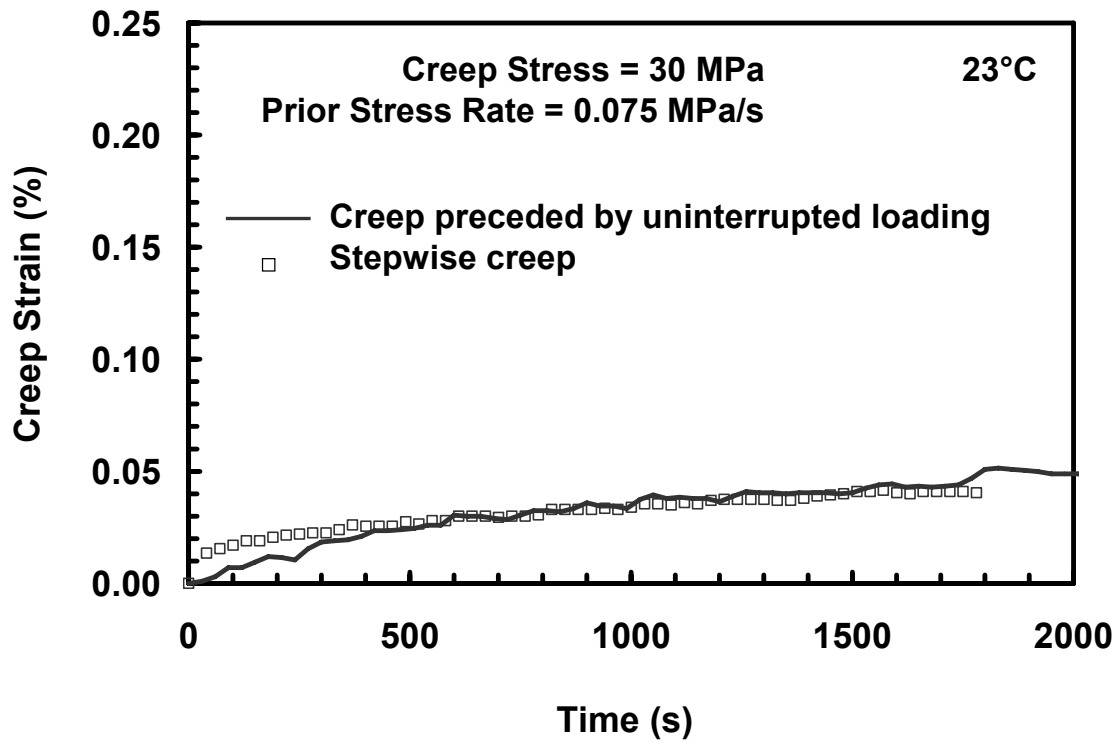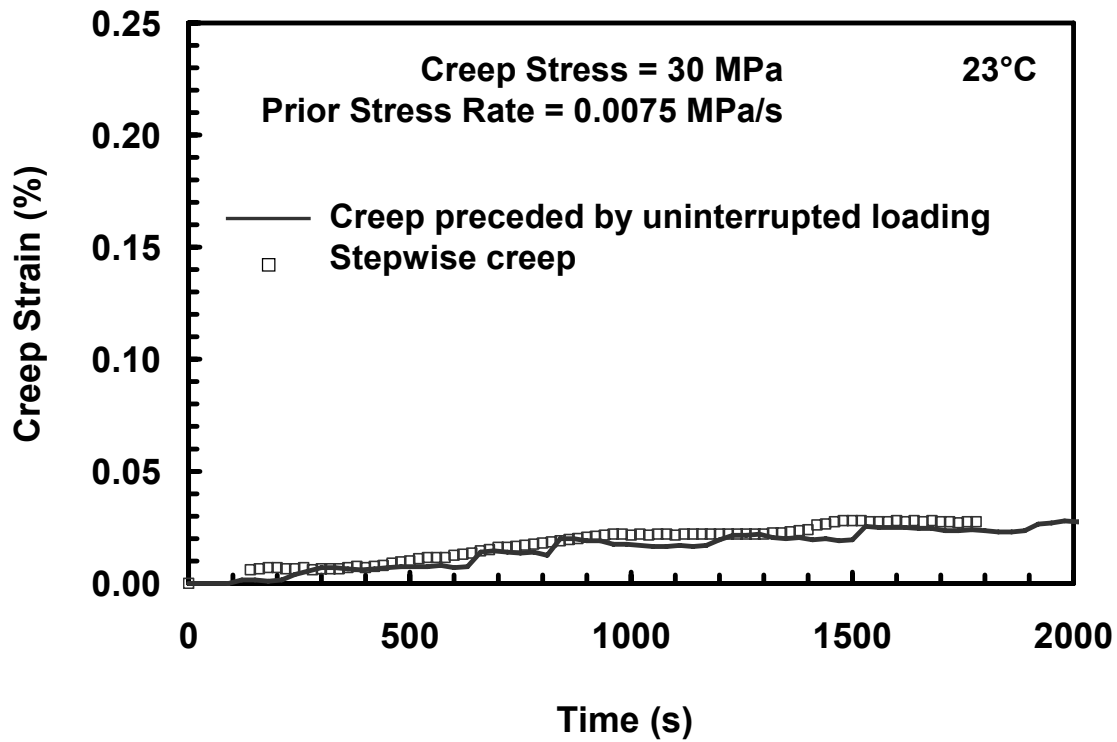
Figure 25. Creep curves obtained at 30 MPa in stepwise creep test and creep test preceded by uninterrupted loading for stress rate of 0.0075 MPa/s at 23ºC

Results of the stepwise creep test performed at 288°C with the loading rate of 0.75 MPa/s are presented in Figs. 26, 27 and 28. It is seen that the stress-strain as well as creep response during loading is qualitatively similar to that at 23°C. As expected larger creep strains are accumulated at elevated temperature at a given stress level. As at 23°C, creep strain accumulated at 25 MPa exceeds that accumulated at a higher stress of 30 MPa. This "anomaly" can again be explained within the framework of the VBO. The overstress would be higher at the start of the 25 MPa creep test than at the start of the 30 MPa creep period. At 288°C, this observation is further supported by evidence in Fig. 27, where creep strain accumulated at 25 MPa in a stepwise creep test is shown together with that obtained in a 25 MPa creep test preceded by uninterrupted loading. The higher overstress

at the 25 MPa point in the uninterrupted stress-strain curve would result in higher creep

rate and creep strain accumulation in a given time seen in Fig.26.
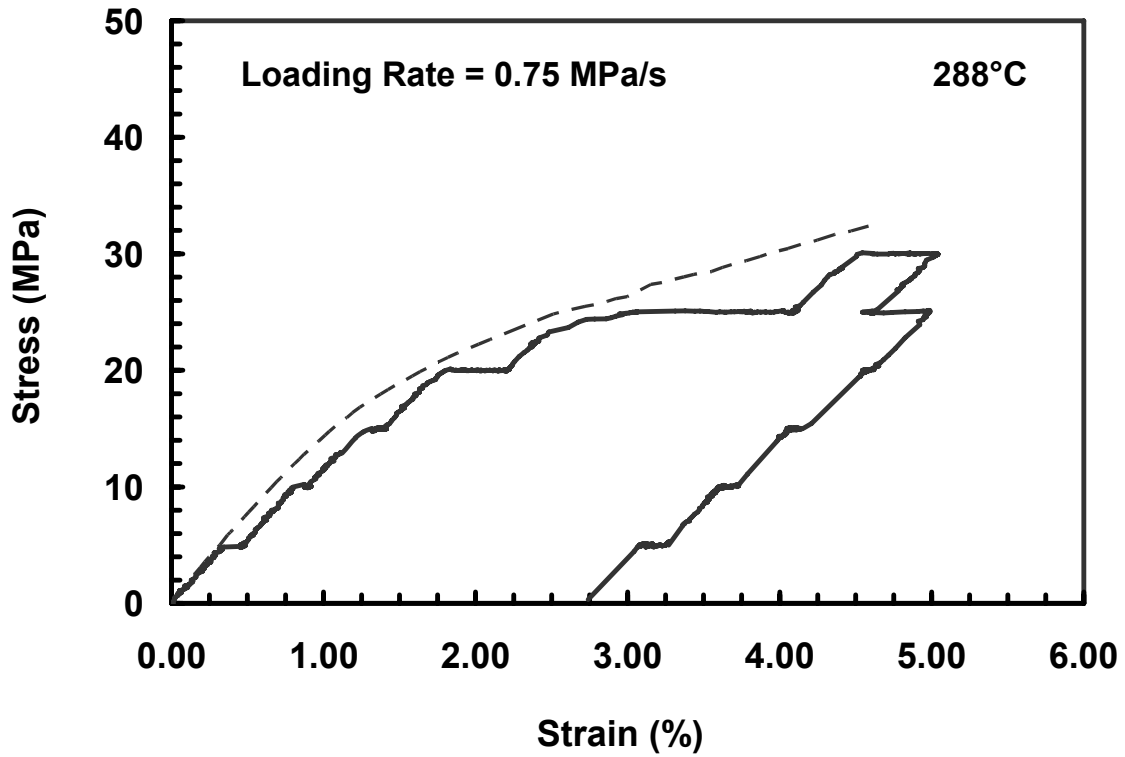
Figure 26. Stress controlled test at rate 0.75 MPa/s with intermittent creep periods of 1800 s duration at 288°C. Similar to that of 23˚C only more pronounced. Also see strain rate reversal at 25 MPa upon unloading
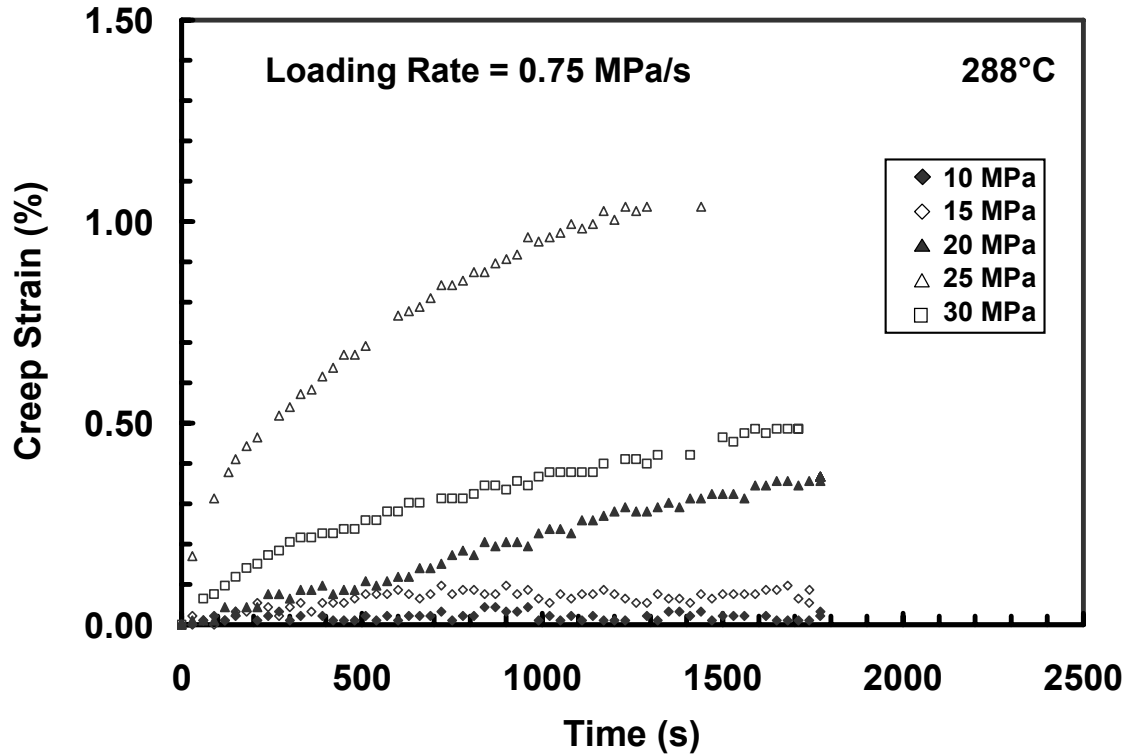
Figure 27. Creep curves upon loading pertaining to the test shown in Fig. 26

Creep tests performed during unloading at 288°C (Fig. 28) demonstrate the rate-reversal effect. At 25 MPa the change in strain during creep is initially negative, but becomes positive after some time. The rate-reversal phenomenon observed in creep during unloading has been reported in literature for the unloading creep/relaxation behavior of polymers at 23°C (Khan, 2002:81,82).

At 20 MPa, creep is negative. As at 23°C, the subsequent creep periods produce larger decrease in strain with decreasing creep stress level. The decrease in strain in the 5 MPa creep test exceeds that produced at 20 MPa by 0.18%.
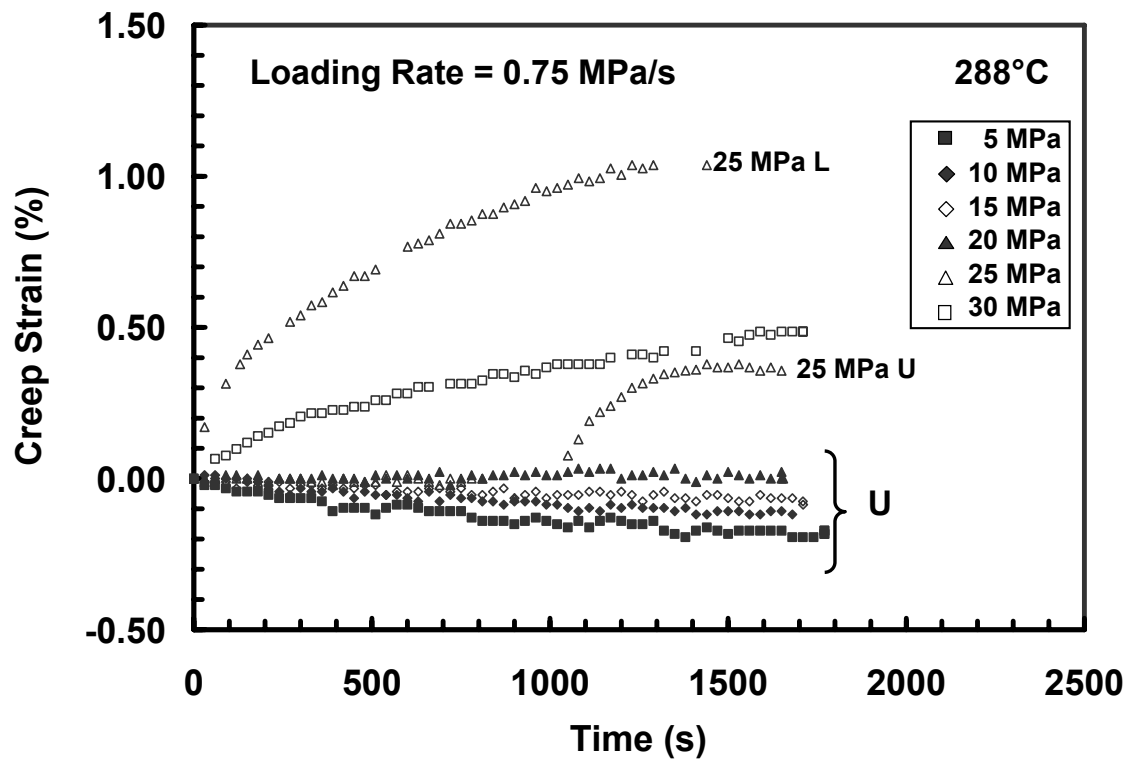
Figure 28. Creep curves upon unloading pertaining to the test shown in Fig. 26
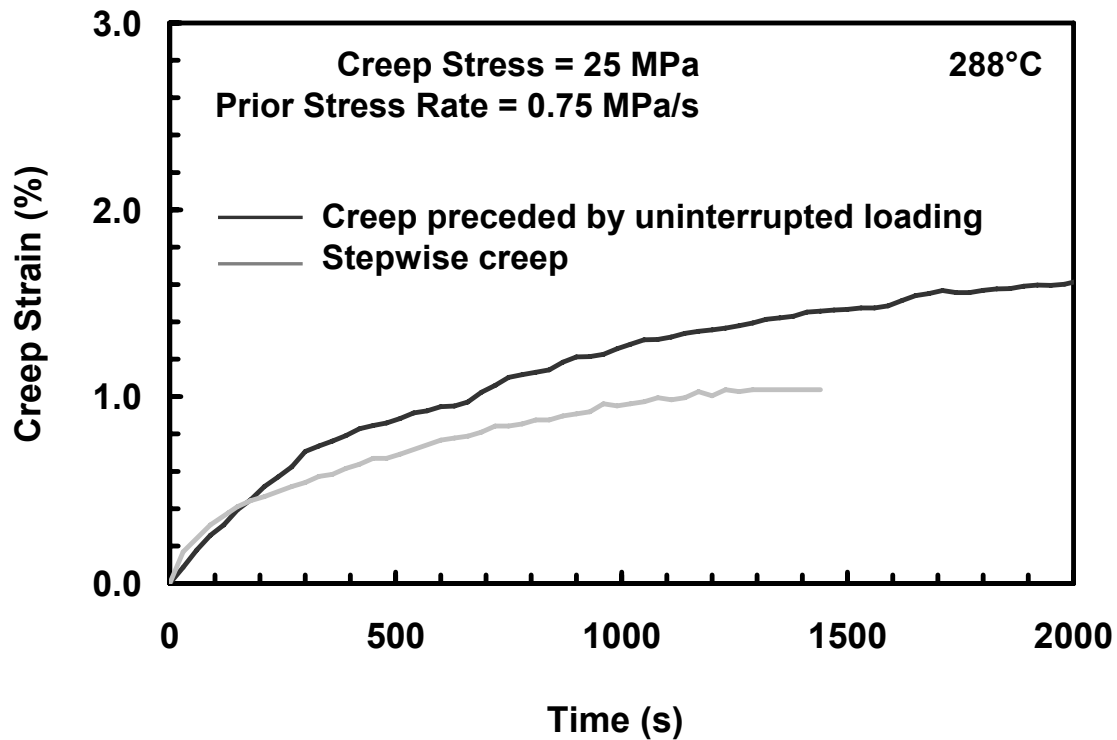
Figure 29. Creep curves obtained at 25 MPa in stepwise creep test and creep test preceded by uninterrupted loading for stress rate of 0. 75 MPa/s at 288°C

The high temperature stepwise creep tests performed with stress rates of 0.075 MPa/s and 0.0075 MPa/s were qualitatively similar to the stepwise creep test performed at 0.75 MPa/s. As seen with the room temperature tests, the only difference between the test with the fast rate and the tests with the slower rates is that there was less creep strain accumulation. Both of the tests at slower rates showed a steady increase in creep strain accumulation with stress upon loading, the rate reversal effect during the first creep period upon unloading, and increasing negative strain with decreasing stress upon unloading.

Recovery

The results for the recovery tests at zero stress performed at 23ºC are shown in Fig.30. For these tests, the stress was monotonically loaded to 30 MPa, then unloaded at rates 0.75 MPa/s, 0.075 MPa/s and 0.0075 MPa/s, then recovered at zero stress for 12 hours. The recovered strain is calculated as the percent of the strain at the beginning of recovery. Note the strain values at the beginning of recovery. These are extremely small strains: hundredths of a percent. These values are so small, they may be below the accuracy level of the extensometer. Therefore, room temperature recovery produces no meaningful data and is not recommended in future experiments.

On the other hand, recovery at 288ºC produced very meaningful results. It has already been seen that this material produces higher strains at high temperature, so the strain at the beginning of recovery for all three tests is well within the accuracy of the extensometer. High temperature recovery does exhibit rate effect. Similar to high temperature creep, higher stress rates recover more strain. The recovery curve of the test performed with the rate of 0.0075 MPa/s is much lower than the other two curves. It only recovered 30% of the initial strain as opposed to 65% and 60% strain recovered at the rates of 0.75 MPa/s and 0.075 MPa/s respectively. It is easy to see that the relationship between stress rates and recovery is not linear.
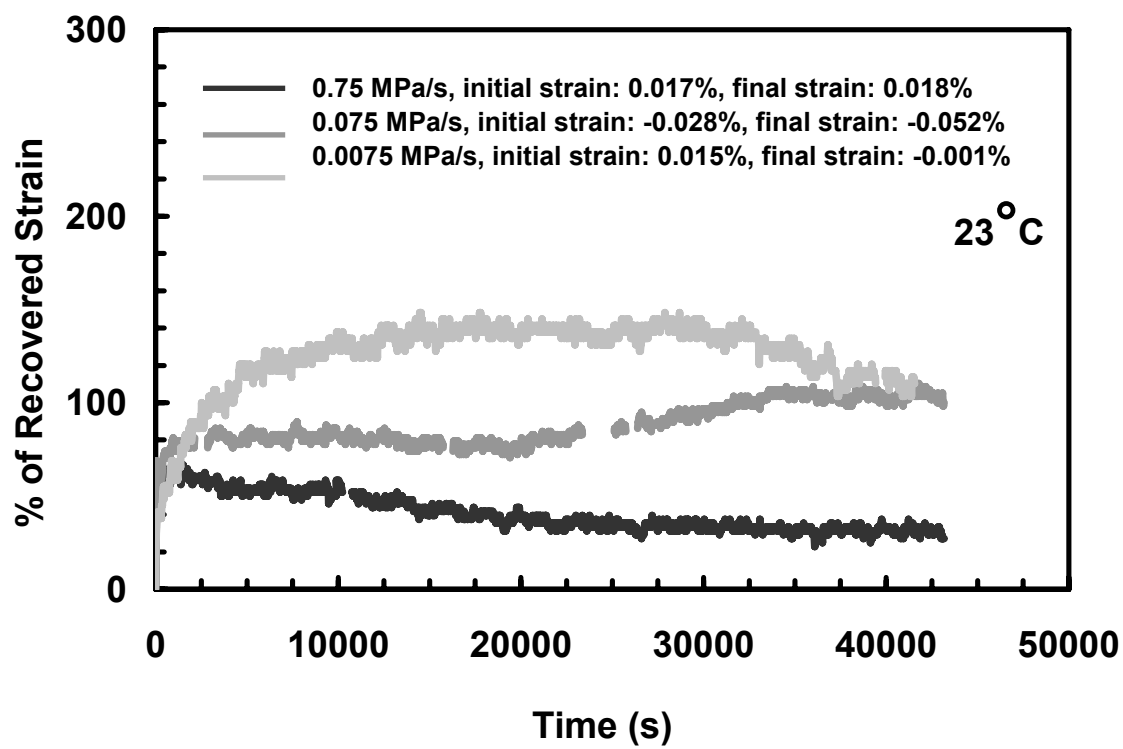
Figure 30. Recovery as percent of strain at beginning of recovery for 23ºC
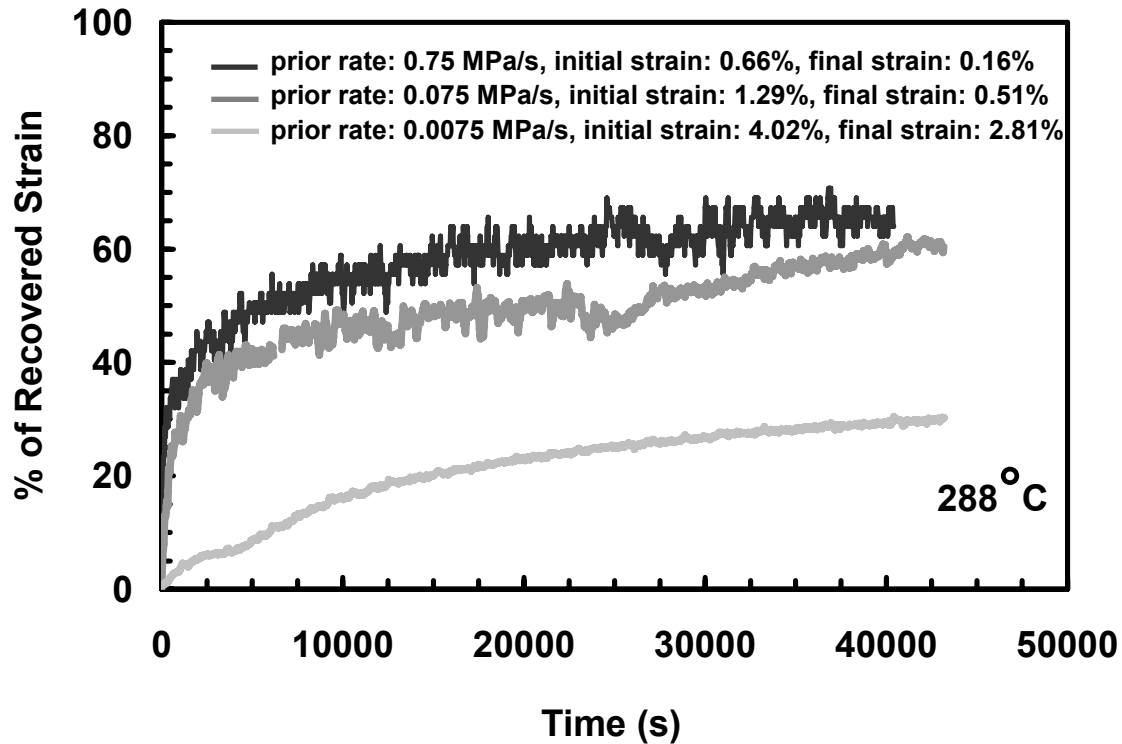
Figure 31. Recovery as percent of strain at beginning of recovery for 288ºC

The recovery tests following monotonic loading and unloading and following stepwise creep both conducted with a stress rate of 0.75 MPa/s and at temperature 288ºC are shown in Fig 32. Notice that the test following stepwise creep recovered much less strain than the test following monotonic loading and unloading. The strain value at the beginning of recovery following the monotonic test is much less than the strain value at the beginning of recovery following the stepwise creep test. This may mean that recovery not only depends on rate, but also on the strain value at the beginning of recovery. Also, remember that upon unloading, during the stepwise creep test, the creep strain accumulations were negative, meaning that much of the strain that would have been recovered at zero stress was already being recovered during unloading.

46

Figure 32. Recovery following monotonic loading and unloading test and recovery following stepwise creep test with prior stress rate of 0.75 MPa/s at 288ºC. Recovery is calculated as the percent of the strain at the beginning of recovery.
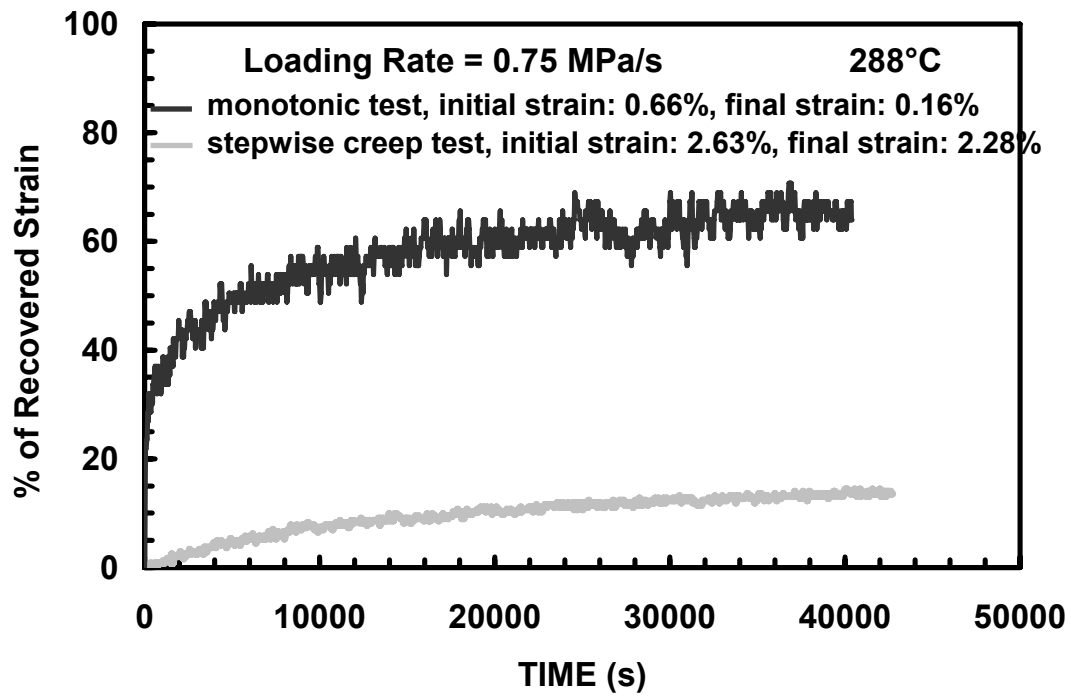
IV. Concluding Remarks

Results have shown that rate dependence does have some affect on the behavior of this material. At room temperature, the stress-strain relationship has little dependence on rate in the elastic region, but has significant rate dependence after the transition to the inelastic region. The effect of rate dependence is non-linear. On the other hand, rate has no significant effect on the stress-strain relationship for the material at 288ºC.

The effect of prior stress rate on creep behavior proceeded by uninterrupted loading was quite the opposite. There was no effect of rate on creep at 23ºC. The creep curves were almost identical for each rate. It is worthy to note that very little creep strain was accumulated at 23ºC (on the order of a tenth of a percent). The creep strain accumulated at 288ºC was much higher and did increase non-linearly with increasing stress rate.

Similar to the creep tests, at room temperature, recovery was very small. The values were so small in fact that they did not warrant confidence in the results. However, the recovery tests at high temperature did create meaningful results. They showed that recovery as a percent of the initial strain at the beginning of recovery increased non-linearly as the prior unloading stress rate increased.

In stepwise creep tests, creep was observed within the quasi-elastic region in both 23 and 288ºC. At both temperatures, creep strain accumulation increased as the stress increased with exception of some instances where the effect of overstress was observed in which case there was more creep strain accumulated at lower stresses. Upon unloading, creep strain was negative for each creep period, and became more negative as

the stress decreased. At 288ºC these effects were more pronounced. The tests at 288ºC exhibited one feature not observed at 23ºC. For the first creep period upon unloading, a rate reversal effect was observed. The creep strain rate would at first be negative, then become positive.

Bibliography

Bordonaro, C. M. and E. Krempl. "The Effect of Strain Rate on the Deformation and Relaxation Behavior of 6/6 Nylon at Room Temperature," *Polymer Engineering and Science,* 32: 1066-1072 (August 1992).

Colak, Ozgen U. "Modeling deformation behavior of polymers with viscoplasticity theory based on overstress," *International Journal of Plasticity,* 21:145-160 (2005).

Cook, Robert D. and others. *Concepts and Applications of Finite Element Analysis.* Hoboken, NJ: John Wiley & Sons, Inc., 2002.

Findley, William N. and others. *Creep and Relaxation of Nonlinear Viscoelastic Materials.* Mineola, NY: Dover Publications, Inc., 1989.

Ho, Kwangsoo and Erhard Krempl. "Extension of the viscoplasticity theory based on overstress (VBO) to capture non-standard rate dependence in solids," *International Journal of Plasticity,* 18: 851-872 (2002).

Khan, Fazeel. *The Deformation Behavior of Solid Polymers and Modeling with the Viscoplasticity Theory Based on Overstress.* PhD dissertation. Rensselaer Polytechnic Institute, Troy NY, 2002.

Khan, Fazeel and Erhard Krempl. "Amorphous and Semicrystalline Solid Polymers: Experimental and Modeling Studies of Their Inelastic Deformation Behaviors," *Journal of Engineering Materials and Technology,* (In Press).

Khan, Fazeel and Erhard Krempl. "Pre-Necking and Post-Necking Relaxation and Creep Behavior of Polycarbonate: A Phenomenological Study," *Polymer Engineering and Science,* 44:1783-1791 (September 2004).

Krempl, Erhard. "Some general properties of solid polymer inelastic deformation behavior and their application to a class of clock models," *Journal of Rheology,* 42 (4):713-725 (July/August 1998).

Krempl, Erhard and Christine M. Bordonaro. "A State Variable Model for High Strength Polymers," *Polymer Engineering and Science,* 35: 310-316 (February 1995).

Krempl, E. and C. M. Bordonaro. "Non-Proportional Loading of Nylon 66 at Room Temperature," *International Journal of Plasticity,* 14: 245-258 (1998).

Krempl, Erhard and Fazeel Khan. "Rate (time)-dependent deformation behavior: an overview of some properties of metals and solid polymers," *International Journal of Plasticity,* 19:1069-1095 (2003).

McClintock, Frank A. and others. *Mechanical Behavior of Materials.* Reading MA: Addison-Wesley Publishing Company, Inc., 1966.

Rabotnov, Yu. N. *Creep Problems in Structural Members.* Amsterdam: North-Holand Publishing Company, 1969.

Ruggles, M.B. "Experimental Investigation of Uniaxial and Biaxial Rate-Dependant Behavior of a Discontinuous Metal-Matrix Composite at 538°C," *Composites Science and Technology,* 57:307-318 (1997).

Ruggles, M.B. and E. Krempl. "Rate Sensitivity and Short-Term Relaxation Behavior of AISI Type 304 Stainless Steel at Room Temperature and at 650°C; Influence of Prior Aging," *Journal of Pressure Vessel Technology,* 113:385-391 (August 1991).

Ruggles, M.B. and others. "The Rate-Dependent Mechanical Behavior of Modified 9wt.%Cr-1wt.%Mo steel at 538°C," *Materials Science and Engineering,* A186:15-21 (1994).

Ruggles-Wrenn, M.B., J.M. Corum, and R.L. Battiste. "Short-term static and cyclic behavior of two automotive carbon-fiber composites," *Composites: Part A,* 34:731-741(2003).

Zhang, Chuntao and Ian D. Moore. "Nonlinear Mechanical Response of High Density Polyethylene. Part I: Experimental Investigation and Model Evaluation," *Polymer Engineering and Science,* 37: 404-413 (February 1997).

Appendix

The content of this section is an example of viscoelastic mathematical modeling based on the Standard Linear Solid shown in Fig. 1.

The elongation of the first spring is represented by

$$\varepsilon_1 = \frac{\sigma}{E_1}.$$

(1)

The elongation of the Kelvin-Voigt element is related to the stress by

$$\sigma = E_2 \varepsilon_2 + \eta \dot{\varepsilon}_2.$$

(2)

The total elongation is

$$\varepsilon = \varepsilon_1 + \varepsilon_2.$$

(3)

The differential equation

$$\left(\frac{1}{E_1} + \frac{1}{E_2} \right) \sigma + \frac{\eta}{E_1 E_2} \dot{\sigma} = \varepsilon + \frac{\eta}{E_2} \dot{\varepsilon}$$

(4)

is the result of eliminating ε_1 and ε_2.

The following substitutions are made in order to simplify the problem:

$$E_1 = E$$

(5)

$$\frac{E_1 + E_2}{\eta} = \lambda$$

(6)

$$\frac{E_2}{\eta} = \mu \tag{7}$$

And the resulting equation is

$$\dot{\sigma} + \lambda\sigma = E(\dot{\varepsilon} + \mu\varepsilon) \tag{8}$$

If a load is applied rapidly so that $\dot{\sigma}$ is large, it follows that $\dot{\varepsilon}$ will be large, and σ and ε negligibly small. Then, E is the instantaneous modulus of elasticity. On the other hand, if the load is applied very slowly so that $\dot{\sigma}$ and $\dot{\varepsilon}$ are negligibly small, then $E(\mu/\lambda)$ is the long-term modulus of elasticity. If a load is suddenly applied, then held constant for some time (creep), then the original deformation is given by the instantaneous modulus, but as the deformation increases during the creep period, the deformation corresponds to the long-term modulus.

Solving equation (8), and assuming that ε is a given function of time, the integral of the homogeneous equation is

$$\sigma = Ce^{-\lambda t}. \tag{9}$$

Applying the method of variation of parameters results in

$$C = E\int_{-\infty}^{t}(\dot{\varepsilon} + \mu\varepsilon)e^{\lambda\tau}d\tau \tag{10}$$

or

$$C = E\left[\varepsilon(t)e^{\lambda t} - (\lambda - \mu)\int\limits_{-\infty}^{t} \varepsilon(\tau)e^{\lambda \tau}d\tau \right]. \qquad (11)$$

Then the stress can be expressed in terms of the deformation as

$$\sigma = E\left[\varepsilon - (\lambda - \mu)\int\limits_{-\infty}^{t} \varepsilon(\tau)e^{-\lambda(t-\tau)}d\tau \right]. \qquad (12)$$

Or the deformation can be expressed in terms of the stress as

$$\varepsilon = \frac{1}{E}\left[\sigma + (\lambda - \mu)\int\limits_{-\infty}^{t} \sigma(\tau)e^{-\mu(t-\tau)}d\tau \right] \qquad (13)$$

(Rabotnov, 1969).

1. REPORT DATE *(DD-MM-YYYY)* Sep 2005	2. REPORT TYPE **Thesis**	3. DATES COVERED *(From – To)* Sep 2004-Sep 2005
4. TITLE AND SUBTITLE Rate Dependence and Short Term Creep Behavior of PMR-15 Neat Resin at 23 and 288°C		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Candice M. Westberry		**5d. PROJECT NUMBER**
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S) Air Force Institute of Technology Graduate School of Engineering and Management (AFIT/ENY) 2950 Hobson Way WPAFB OH 45433-7765		**8. PERFORMING ORGANIZATION REPORT NUMBER** AFIT/GAE/ENY/05-S07
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. R.B. Hall and Dr. G.A. Schoeppner AFRL/MLBCM 2941 Hobson Way WPAFB, OH 45433		**10. SPONSOR/MONITOR'S ACRONYM(S)**
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.		
13. SUPPLEMENTARY NOTES		

14. ABSTRACT

This research focuses on experimental investigation of rate-dependent behavior and short-term creep of PMR-15 neat resin at 23 and 288°C. Effect of loading rate on monotonic stress-strain behavior was explored in monotonic tests at constant stress rates of 0.75, 0.075, and 0.0075 MPa/s at 23 and 288°C. In addition, effect of prior stress rate on creep behavior was explored in creep tests preceded by uninterrupted loading to a target stress. At each temperature three creep tests were conducted for a given stress level, where loading rate was changed from test to test. Creep stress levels were 30 and 25 MPa at 23 and 288°C, respectively. Also, the effect of stress and strain at the beginning of the creep period was studied in stepwise creep tests, where specimens were subjected to a constant stress rate loading with 1800 s creep periods at 5 MPa stress intervals. Specimens were loaded to a maximum stress then unloaded to zero stress, with creep periods during loading and unloading. Finally, the effect of loading rate was studied in recovery tests where specimens were monotonically loaded to 30 MPa and unloaded to zero MPa, then recovered for 12 hours.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dr. Marina Ruggles-Wrenn ENY
a. REPORT **U**	**U**	**U**	**UU**	66	**19b. TELEPHONE NUMBER** *(Include area code)* 937-255-3636 x4641